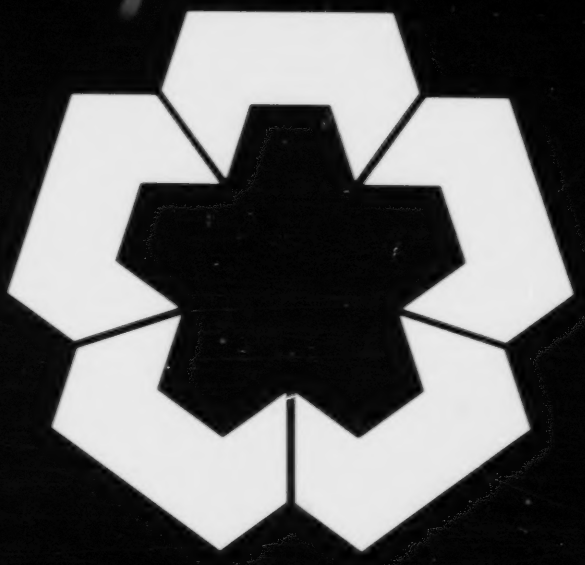

Sulphur Isotope Abundances In the Environment and Their Relation to Long-Term Sour Gas Flaring, Near Valleyview, Alberta

RMD Report 83/18

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SULPHUR ISOTOPE ABUNDANCES IN THE ENVIRONMENT AND THEIR RELATION TO LONG TERM SOUR GAS FLARING, NEAR VALLEYVIEW, ALBERTA

RESEARCH MANAGEMENT DIVISION
and
POLLUTION CONTROL DIVISION
AIR QUALITY CONTROL BRANCH
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FINAL REPORT

SULPHUR ISOTOPE ABUNDANCES IN THE ENVIRONMENT AND THEIR RELATION TO LONG TERM SOUR GAS FLARING, NEAR VALLEYVIEW, ALBERTA

by

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SUMMARY

Well over 300 samples, consisting of stack gas, ambient air (SO_2 and particulate matter), rain, surface waters, soil, vegetation, crop seeds, and fertilizers in the Valleyview area of Alberta, were analysed for their sulphur concentration and isotopic abundance. Changes in pH upon addition of acid were used to crudely assess the buffering properties of selected soil horizons.

Sulphur emissions from the Amerada-Hess Gas Plant flaring operations (now inactive) were found to be enriched in the heavier stable sulphur isotope ^{34}S, with an average $\delta^{34}S$ value of +17‰. The soil horizons in the area were relatively depleted in ^{34}S ($\delta^{34}S \approx -12$ ‰)[1]. This soil value is interpreted to represent the pre-industrial isotopic composition of the environment. The situation was very favourable for utilizing $\delta^{34}S$ values to evaluate the industrial contribution of sulphur to the environment in this area.

This study was initiated to explore the applicability of stable sulphur isotope measurement techniques for detecting and quantifying possible alterations in the distribution of sulphur in the environment, as a result of industrial emissions. This investigation was not designed to examine the environmental consequences of any observed alterations in the distribution of sulphur. Since many facets of the environment (air, water, soil, and vegetation) were examined, the numbers of samples for some facets were restricted. Hence, some of the trends observed are based on too few data.

The concentrations and $\delta^{34}S$ values of atmospheric SO_2 and particulates were found to depend strongly upon wind direction measured near the ground level. Identification of sources on the basis of these data is difficult without a detailed knowledge of upper wind behaviour. While the flare was operative, $\delta^{34}S$ values for atmospheric particulates and SO_2, especially at their high concentrations, approached those

[1] See definition of $\delta^{34}S$ value, page 3.

measured for the emissions (Figures 10 and 11). After flaring ceased, the $\delta^{34}S$ values of both atmospheric SO_2 and particulates were lower (Figure 12).

$\delta^{34}S$ values comparable to those of the emissions were detected in some rain samples. The rain sampling procedure, however, did not exclude the contributions of dry deposition. Therefore, in reality these were composite wet and dryfall samples.

Lower concentrations of total sulphur in surface waters were identified with $\delta^{34}S$ values typical of deep soil horizons, while higher concentrations were identified with $\delta^{34}S$ values similar to those of the emissions (Figure 14).

The pH of the Ae soil horizon was found to decrease with increasing soluble sulphur concentration, with the exception of Site 2 which was closest to the stack (Figure 15). While upper soil horizons were acidic, the C horizon was neutral to basic. With the addition of H_2SO_4 (2 H^+ meq/100 g soil), the pH of samples from the upper soil horizons typically decreased by two units. In contrast, the C horizon samples maintained a nearly constant pH (near 8) with H_2SO_4 additions up to 12 H^+ meq/100 g soil. Differences in titration curves from site to site are difficult to relate to the sulphur concentrations and the isotope data.

The concentration of soluble sulphur in the Ae horizon generally decreased with distance from the stack. Two study sites, however, were anomalous and were characterized by very porous soils (Figure 20).

The $\delta^{34}S$ values of soluble sulphur in the uppermost LFH horizon tended to increase with the concentration of the sulphur fraction (Figure 19), while in lower horizons higher sulphur concentrations were identified with more negative $\delta^{34}S$ values (Figure 21). The more positive $\delta^{34}S$ values of the LFH indicate the input of industrial sulphur while the more negative $\delta^{34}S$ values of the lower soil horizons identify natural subsurface sources.

The $\delta^{34}S$ values of most soil horizons increased with proximity to the flare stack (Figure 26). We conclude that at distances closer

than 5 km, industrial sulphur has penetrated as deeply as the C horizon and elevated the $\delta^{34}S$ values by at least 5 $^{o}/_{oo}$. Simple isotopic-mass balance calculations were carried out which assumed that the $\delta^{34}S$ values of all horizons prior to flaring were -10 $^{o}/_{oo}$. On this basis, at sites closer than 5 km to the stack, we calculate that about one-third of the sulphur in the C horizon was derived from the industry.

The same calculations indicate that the soluble sulphur in the uppermost LFH layer is primarily of industrial origin near the stack while at 10 km distance the industrial component drops to about 50 percent. The industrial contribution to total sulphur in the LFH horizon is slightly less than for soluble sulphur, reaching about 80 percent within 2 km of the stack.

Tree lichens, farther away from the stack, had lower soluble sulphur concentrations than those which were closer (Figure 30).

The $\delta^{34}S$ values of aspen leaves tended to decrease with distance from the stack (Figure 32). However, since both the concentrations and $\delta^{34}S$ value differed with the time of the year, more sampling is needed to better establish the trends.

While the results obtained in this study demonstrate uptake of industrially-derived sulphur by the soil and native vegetation (lichens, aspen, moss), negative $\delta^{34}S$ values signified that industrial sulphur was a minor component in crop seeds.

The sulphur concentrations and isotopic data reveal that: 1) the pre-industrial environments of the Teepee Creek and Valleyview areas of Alberta were very similar; and 2) substantial quantities of sulphur from flaring operations were present in the atmosphere, hydrosphere, biosphere, and pedosphere at Valleyview.

A number of recommendations emerge from this study. Some pertain specifically to the Valleyview and Teepee Creek areas, while others have wide implications for improvements in methodology and future environmental research in Alberta.

The recommendations are best expressed as four major statements with auxiliary recommendations. The specific recommendations are:

1. Emphasize co-ordinated multidisciplinary studies of pollution effects.
   - 1.1 A multidisciplinary approach should be used to gather data to characterize the existing environment prior to establishing or expanding sour gas processing plants. Equivalent data should be obtained for comparison every three to five years throughout the life of the plant and for some time thereafter, as dictated by the data.
   - 1.2 The Teepee Creek area should be re-examined within the next three years and the Valleyview area should also be re-examined within the next five years.
   - 1.3 Data gaps in the comparison of Teepee Creek and Valleyview should be eliminated where possible.
   - 1.4 Application of new and relevant methodologies should be considered in meeting the above recommendations.
2. Examine the effects of sour gas processing plant emissions on soil chemistry and microbiology.
   - 2.1 Acceptable laboratory procedures for assessing long-term effects of sour gas plant emissions on the soil buffering capacity must be developed.
   - 2.2 Buffering mechanisms of Alberta soils should be identified and documented.
   - 2.3 Examine how current agricultural practices relate to the effects of industrial emissions on soil properties and productivity.
   - 2.4 The isotopic compositions of sulphur-containing soil constituents should be investigated in detail.
3. Examine the disposition of sulphur compounds in vegetation in relation to productivity.
   - 3.1 The isotopic composition of sulphur-containing plant constituents should be investigated in detail.

3.2 The variation over time of sulphur content and isotopic composition in vegetation should be documented.

3.3 Mechanisms of sulphur incorporation and translocation within plants should be explored.

4. Increase the efficiency of sampling atmospheric sulphur compounds.

4.1 The selection of air sampling sites should be based on the results of a preliminary biomonitoring survey for pollution-sensitive species.

4.2 Increase the efficiency and flexibility of the existing wind directionally controlled sampling systems.

4.3 Automated precipitation collecting devices should be used so that they remain open only during wetfall or only during dryfall.

TABLE OF CONTENTS

		Page
SUMMARY		
LIST OF TABLES		
LIST OF FIGURES		
ACKNOWLEDGEMENTS		
1.	INTRODUCTION	1
1.1	Objectives of the Study	1
1.2	Fundamentals of Stable Isotope Studies	2
2.	THE STUDY AREA	10
2.1	Location and Size	10
2.2	Physiography and Soils	10
2.3	Vegetation	10
2.4	History of the Amerada-Hess Facility	10
3.	MATERIALS AND METHODS	13
3.1	Sampling of Production Well Gases	13
3.2	Atmosphere	13
3.2.1	High Volume (Hi-Vol) Sampling Array	14
3.2.2	Integrated Sampling	14
3.2.3	Sample Collection	14
3.3	Rain (Bulk Wet and Dryfall Samples)	15
3.4	Surface Water	15
3.5	Soil	16
3.5.1	Soil Sampling	16
3.5.2	Soil pH	17
3.5.3	Soil Sulphur Content	17
3.5.4	Soil Buffering Capacity	17
3.6	Vegetation	17
3.6.1	Sulphur Extraction from Vegetation	18
3.7	Fertilizer	18
3.8	SIRA (Stable Isotope Relative Abundances Analysis)	18
3.8.1	Sulphur Dioxide Preparation	19
3.8.2	Mass Spectrometry	19
4.	RESULTS AND DISCUSSION	20
4.1	Production Well Gases	20
4.2	Atmosphere	20
4.3	Rain	30
4.4	Surface Water	33
4.5	Soil	33
4.5.1	The pH Values of Soil	33

TABLE OF CONTENTS (CONTINUED)

		Page
4.5.2	Buffering Capacity	35
4.5.3	Soil Sulphur Concentrations and $\delta^{34}S$ Values	37
4.6	Vegetation	52
4.6.1	Epiphytic Lichens	52
4.6.2	Aspen (*Populus tremuloides*)	55
4.6.3	Ground Lichens and Mosses	59
4.7	Fertilizers	59
4.8	Produced Crop Seed	61
5.	CONCLUSIONS	62
6.	COMPARISON OF THE VALLEYVIEW AND TEEPEE CREEK STUDIES	65
7.	RECOMMENDATIONS	68
8.	REFERENCES CITED	72
9.	APPENDICES	74
9.1	Amerada-Hess Gas Production Figures, 1952 to 1979	74
9.2	Locations of Sample Collection Sites in the Valleyview Area, Alberta	77
9.3	Resume of Soils by Pedology Consultants	78
9.3.1	General Comments Regarding Soils	78
9.3.1.1	Parent Materials	78
9.3.1.2	Permeability	78
9.3.1.3	Soil Sampling	82
9.3.2	Comparison of Valleyview Area Soils with Teepee Creek Soils	82
9.4	Typical Plant Species Found in Trembling Aspen Communities	82
9.5	$\delta^{34}S$ Values and Sulphur Concentrations for SO_2 and Suspended Particulate Matter Sampled in the Valleyview Area, Alberta, 1980	85
9.6	Sulphur Concentrations and $\delta^{34}S$ Results for Bulk Rain Samples Collected in the Valleyview Area, Alberta, Summer 1980	94
9.7	Sulphur SIRA Results for Surface Water Samples Collected in the Valleyview Area, Alberta, Summer 1980	96
9.8	pH, Sulphur Concentrations and SIRA Results for Soils, Valleyview Area, Alberta (Summer 1980)	98
9.9	Buffering Capacities of Soils, Valleview Area, Alberta, Summer 1980	102

TABLE OF CONTENTS (CONCLUDED)

		Page
9.10	Sulphur SIRA Results of the Analysis of *Parmelia sulcata* and Other Epiphytic Lichens, Trembling Aspen Foliage, Fertilizers, and Crops in the Valleyview Area, Alberta	105

LIST OF TABLES

		Page
1.	Comparison of Mean $\delta^{34}S$ Values for Environmental Constituents in the Teepee Creek and Valleyview Areas of Alberta	67
2.	Gas Production at Battery 16-31-71-23 W5M, Amerada-Hess Sturgeon Lake Plant	75
3.	Gas Production at Battery 10-29-71-23 W5M, Amerada-Hess Sturgeon Lake Plant	76
4.	Valleyview Area Soil Samples	79
5.	$\delta^{34}S$ Values and Sulphur Concentrations for SO_2 and Suspended Particulate Matter Sampled at the Dallman Farm, Approximately 15 km NNW of Valleyview, Alberta, 1980 May 27 to June 07	86
6.	$\delta^{34}S$ Values and Sulphur Concentrations for SO_2 and Suspend Particulate Matter Sampled at the Melenius Farm, Approximately 14 km N of Valleyview, Alberta, 1980 June 07 to 14	87
7.	$\delta^{34}S$ Values and Sulphur Concentrations for SO_2 and Suspended Particulate Matter Sampled at the Gourlay Farm, Approximately 14 km N of Valleyview, Alberta, 1980 June 18 to 24	88
8.	$\delta^{34}S$ Values and Sulphur Concentrations for SO_2 and Suspended Particulate Matter Sampled at the Halibisky Farm, Approximately 15 km W of Valleyview, Alberta, 1980 June 24 to July 03	89
9.	$\delta^{34}S$ Values and Sulphur Concentrations in SO_2 and Suspended Particulate Matter Sampled at the Halibisky Farm, Approximately 15 km W of Valleyview, Alberta, 1980 November 09 to 19	90
10.	$\delta^{34}S$ Values and Sulphur Concentrations in SO_2 and Suspended Particulate Matter Sampled at the Dallman Farm, Approximately 15 km NNW of Valleyview, Alberta, 1980 November 25 to 30	91
11.	$\delta^{34}S$ Values and Sulphur Concentrations in SO_2 and Suspended Particulate Matter Collected on the Roof of the Provincial Building, Valleyview, Alberta, 1980 June 17 to July 11	92
12.	$\delta^{34}S$ Values and Sulphur Concentration for SO_2 and Total Suspended Particulates Collected on the Dallman Farm, Approximately 15 km NNW of Valleyview, Alberta, 1980 June 19 to July 19	93

continued ....

LIST OF TABLES (CONCLUDED)

		Page
13.	Sulphur Concentration and $\delta^{34}S$ Results for Bulk Rain Samples Collected in the Valleyview Area, Alberta, Summer 1980	95
14.	Sulphur SIRA Results for Surface Water Samples Collected in the Valleyview Area, Alberta, Summer 1980	97
15.	pH, Sulphur Concentrations, and SIRA Results for Soils, Valleyview, Alberta, Summer 1980	99
16.	Buffering Capacities of Soils, Valleyview, Alberta, Summer 1980	103
17.	Sulphur SIRA Results for *Parmelia sulcata* and Other Lichens Growing on Trembling Aspen in the Valleyview Area, Alberta, Summer 1980	104
18.	Sulphur SIRA Results for Trembling Aspen Collected in the Valleyview Area, Alberta, Summer 1980	107
19.	Sulphur SIRA Data for Ground Lichens and Mosses in the Valleyview Area, Alberta	108
20.	Sulphur SIRA Results for Trace Contaminant Sulphur in Commercial Bulk Fertilizers, Commonly Used in the Valleyview Area, Alberta	109
21.	Sulphur SIRA Data for Crops in the Valleyview Area, Alberta ...	110

LIST OF FIGURES

		Page
1.	Variations in $\delta^{34}S$ Values in Nature	4
2.	Plots Showing the Relationships between $\delta^{34}S$ and Concentrations for a Number of Hypothetical Source Combinations	6
3.	Locations of Sampling Sites in the Valleyview Area	11
4.	Concentrations of Particulates from the High Volume Sampling Array, Dallman Farm	21
5.	$\delta^{34}S$ Values of Particulates from the High Volume Sampling Array, Dallman Farm	22
6.	Concentrations of SO_2 from the High Volume Sampling Array, Dallman Farm	23
7.	$\delta^{34}S$ Values of SO_2 from the High Volume Sampling Array, Dallman Farm	24
8.	$\delta^{34}S$ Values and Concentrations of Particulates and SO_2 from the High Volume Sampling Array, Halibisky Farm, 1980 November 09 to 19	26
9.	$\delta^{34}S$ Values and Concentrations of SO_2 from High Volume Sampling Array, Gourlay Farm, 1980 December 08 to 12	27
10.	$\delta^{34}S$ vs. Concentrations of SO_2, Continuous High Volume Sampling, Dallman Farm, mid-June to mid-July 1980	28
11.	$\delta^{34}S$ vs. Concentrations of Particulate Sulphur, Continuous High Volume Sampling, Dallman Farm, mid-June to mid-July 1980	29
12.	$\delta^{34}S$ vs. Values for Particulates vs. $\delta^{34}S$ Values for SO_2	31
13.	$\delta^{34}S$ vs. Concentration of Total Sulphur in Combined Wet and Dryfall Samples	32
14.	$\delta^{34}S$ vs. Concentration of Total Sulphur in Surface Waters	34
15.	Concentration of Soluble Sulphur vs. pH in Ae Soil Horizon	36

continued ...

LIST OF FIGURES (CONTINUED)

Page

16. Titration Curves Illustrating Buffering Capacity of Soils in the Valleyview Area 38

17. Concentration of Total Sulphur vs. that of Soluble Sulphur in the LFH Horizon 40

18. Concentration of Soluble Sulphur in AE Horizon vs. Distance from the Stack 41

19. $\delta^{34}S$ vs. Concentration of Soluble Sulphur in LFH Horizon 42

20. $\delta^{34}S$ vs. Concentration of Soluble Sulphur in Ae Horizon 43

21. $\delta^{34}S$ vs. Concentration of Soluble Sulphur in the Bt Horizon 44

22. $\delta^{34}S$ vs. Concentration of Soluble Sulphur in the BC Horizon 45

23. $\delta^{34}S$ vs. Concentration of Soluble Sulphur in the C Horizon 46

24. $\delta^{34}S$ for vs. Concentration of Total Sulphur in the LFH Horizon 48

25. $\delta^{34}S$ for Total Sulphur vs. the $\delta^{34}S$ for Soluble Sulphur in the LFH Horizon 49

26. $\delta^{34}S$ Values for Different Soil Horizons as a Function of Distance from the Stack 50

27. $\delta^{34}S$ Values of Different Soil Horizons for Three Sites near and the Three Sites farther away from the Flare Stack 51

28. Concentration of Soluble Sulphur in *Parmelia sulcata* vs. Distance from Stack 53

29. Concentration of Soluble Sulphur in *Hypogymnia physodes* vs. Distance from Stack 54

30. $\delta^{34}S$ for Total Sulphur vs. the $\delta^{34}S$ for Soluble Sulphur in Tree Lichens 56

continued ...

LIST OF FIGURES (CONCLUDED)

Page

31. $\delta^{34}S$ Value of Soluble Sulphur in Aspen Leaves vs. Distance from Stack 57

32. $\delta^{34}S$ Value of Soluble Sulphur in Aspen Leaves vs. Distance from Stack 58

33. $\delta^{34}S$ vs. Concentration of Soluble Sulphur in Aspen Leaves 60

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1. INTRODUCTION

Any industrial or agricultural activity will have an impact on the environment. The generally accepted goal is to minimize that impact to an acceptable limit. The difficulty comes in attempting to reach a consensus as to the definition of "acceptable".

Current air quality standards have been established to prevent acute injury to human health and human welfare (involving such concerns as crops, livestock, machinery, other properties, and the aesthetic appearance and recreational usefulness of the surrounding environment). In recent years, a few scientists have concentrated on LTPECE (Long Term Pollution Exposure Cumulative Effects). It has become abundantly clear that it is not sufficient to prevent the immediate pollution effect, but LTPECE must be considered seriously.

In response to government and public concerns about LTPECE and sulphur dioxide emissions by industry in Alberta, the present exploratory study was initiated to determine how atmospheric sulphur compounds from 24 years of natural gas flaring might have altered the sulphur distribution in the Valleyview environment. It must be stressed that it was not the intent of the authors to study the consequential effects of any such alterations detected.

1.1 OBJECTIVES OF THE STUDY

The primary objectives of this study were to:

1. Generate relevant data to assess the changes in the environmental sulphur distribution caused by operations to date of the Amerada-Hess sour gas processing plant in the Valleyview area of Alberta.
2. Produce data characteristic of the existing environment so that measurements of sulphur content of soil, vegetation, etc. in subsequent years can be related to future industrial activities (or the lack thereof).
3. Compare the environment near Valleyview (where a long-term source of SO_2 emissions has ceased) to the situation at

Teepee Creek, Alberta (where SO_2 emissions recently began from a small source).

4. Determine the extent to which the flaring has increased the sulphur content of the soil, compared to the situation documented previously for the Teepee Creek area.

To meet these overall project objectives, it was desirable to meet the following analytical objectives:

1. Determine the sulphur concentration and isotope abundance of representative samples of ambient SO_2, suspended particulate matter, surface water, precipitation, soil, vegetation, and commercial fertilizers.
2. Measure the pH of precipitation, surface water, and soil samples collected.
3. Monitor meteorological parameters such as wind speed and direction, ambient temperature, relative humidity, and precipitation during sampling periods.
4. Try to relate measurements of sulphur isotopic composition and content in the various samples to industrial and other sulphur sources in the area.

1.2 FUNDAMENTALS OF STABLE SULPHUR ISOTOPE STUDIES

Atoms of a given element are not all the same. Although they will always have the same atomic number (number of protons), they can differ from one another in their number of neutrons and, hence, their total mass number. Atoms with the same atomic number but different mass numbers are termed isotopes of the same element. Because of the universal interest in nuclear energy and nuclear medicine, people generally tend to associate the term isotopes with radioactive isotopes. However, stable isotopes do not involve radioactive transformations and can be used with advantage and safety in environmental studies.

In nature, there are many processes which alter isotopic abundances. Consequently, measurements of stable isotope composition of a specimen can reveal much about its history. Stable isotopes of sulphur are the subject of this project.

Sulphur has four stable isotopes, $^{32}_{16}S$, $^{33}_{16}S$, $^{34}_{16}S$, and $^{36}_{16}S$ which have average abundances of 95.0%, 0.74%, 4.24%, and 0.17%, respectively. Stable Isotope Relative Abundance (SIRA) analysis of sulphur usually utilizes $\delta^{32}S$ and $\delta^{34}S$ because of their higher abundances.

SIRA values are expressed on $\delta^{34}S$ scale, defined as:

$$\delta^{34}S \text{ in } {}^{o}/_{oo} = \left\{ \frac{[\delta^{34}S/\ \delta^{32}S]\ \text{SAMPLE}}{[\delta^{34}S/\ \delta^{32}S]\ \text{STANDARD}} \right\} - 1 \times 1000$$

where $^{o}/_{oo}$ (per mil) = parts per thousand and $[^{34}S/^{32}S]$ is the ratio of the number of ^{34}S atoms to the number of ^{32}S atoms. The standard chosen by international agreement for stable sulphur isotope studies is meteoritic troilite (FeS), specifically from the Canon Diablo Meteorite. This choice arises from consistency in its isotopic composition and the proximity of the meteoritic $\delta^{34}S$ value to the mean of the terrestrial range of δ-values found (Figure 1). A positive $\delta^{34}S$ value means that the sulphur in the samples is more enriched in the heavier ^{34}S than meteoritic troilite, while a negative $\delta^{34}S$ value means that the sample has proportionately less ^{34}S than the meteoritic standard.

As can be seen in Figure 1, sulphate in present-day seawater is markedly uniform in its $\delta^{34}S$ value, near +20 $^{o}/_{oo}$. Results obtained with evaporitic sulphates suggest that there were significant variations in sulphur isotope abundances in the oceans over geological time. Throughout the Devonian period (395 to 345 million years, BP), the oceanic sulphate $\delta^{34}S$ value ranged from +10 to more than +30 $^{o}/_{oo}$. Sour gas in Alberta was derived from ancient oceanic sulphates by various processes and also tends to be enriched in ^{34}S (Krouse 1977b).

Although soils in Alberta range in $\delta^{34}S$ value from -30 $^{o}/_{oo}$ to more than +40 $^{o}/_{oo}$, values near 0 $^{o}/_{oo}$ are frequently encountered (Lowe et al. 1971; Hitchon and Krouse 1972). The more negative $\delta^{34}S$ values have been associated with the Peace River region.

Mosses and lichens (lower plants which lack true roots) tend to acquire sulphur with $\delta^{34}S$ values close to those of atmopsheric sulphur compounds. This is consistent with the fact that these compounds are the

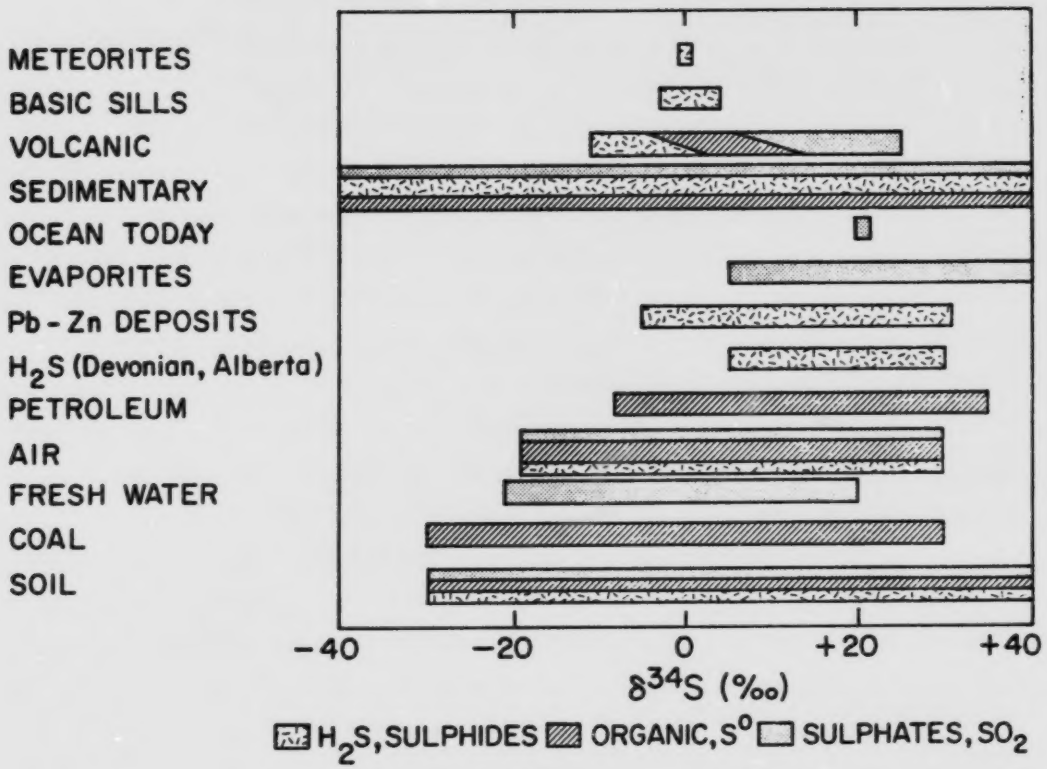

Figure 1. Variations in $\delta^{34}S$ in values in nature.

principal sulphur source for such primitive vegetation. Trees and other plants, which have roots, exhibit $\delta^{34}S$ values intermediate between the soil and the air. This is because these plants acquire sulphur from the soil via their roots, and absorb sulphur compounds from the air directly by their leaves (Krouse 1977a).

Based on the previous discussion, SO_2 emissions related to the gas industry in the Peace River region are predicted to have positive $\delta^{34}S$ values in the range of +15 to +30 o/oo. On the other hand, the vegetation and soils prior to the industrial emissions should have negative $\delta^{34}S$ values. Such trends have been observed at Teepee Creek, Alberta (Krouse and Case 1981).

Relationships between $\delta^{34}S$ values and concentrations are valuable in identifying certain sulphur sources and monitoring the fate of sulphur compounds. Figure 2 (adapted from Krouse 1980) depicts δ-values versus concentration plots for a number of hypothetical source combinations. This is a general analysis, applicable to any element and, in principle, pertains to gases, ions, and fine particulates. Thorough mixing is assumed in the volume of air or water under consideration. The terms "constant" and "variable" refer to the rate of emissions while the isotopic composition of the emissions per se have "fixed" $\delta^{34}S$ values, unless designated as "inhomogeneous."

In the simplest case (Figure 2.1), a sulphur source A is characterized by a constant emission rate and fixed isotopic composition of the emissions. If a steady-state condition exists at an observation site, a plot of δ versus elemental concentration yields a set value. Such an ideal situation is seldom observed except for a short interval of time near a dominant source such as an industrial stack. Figure 2.2 illustrates a source A with a fixed δ-value but a variable emission rate. In the ideal situation the δ-value observed at an observation site remains constant but the concentration varies between a minimum and maximum.

If a source A maintains a constant emission rate but has a variable isotopic composition, the idealized plot (Figure 2.3) is a

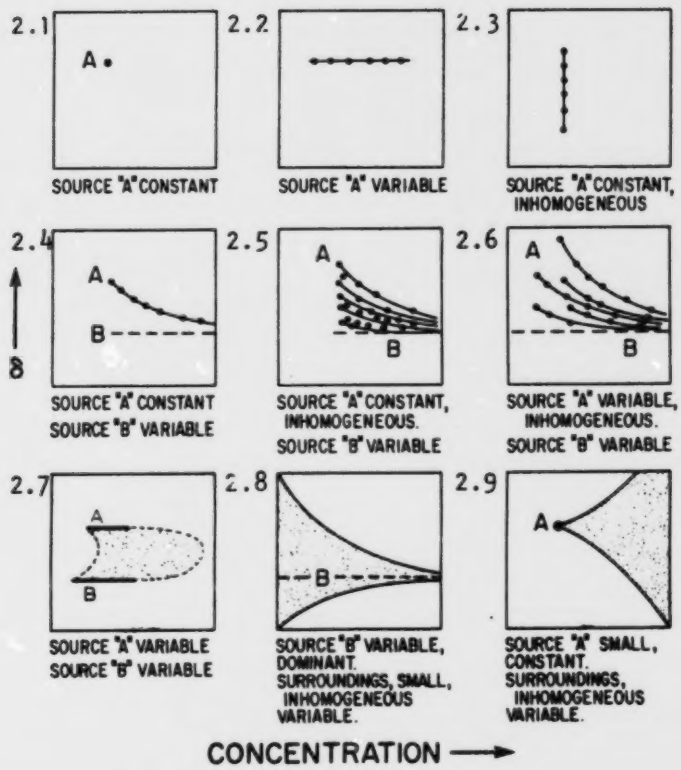

Figure 2. Plots showing the relationships between $\delta^{34}S$ and concentrations for a number of hypothetical source combinations. These models assume simple mixing without any isotopic fractionation. The terms "constant" and "variable" refer to the rate of emission while the term "inhomogeneous" refers to variations in the isotopic composition. Adapted from Krouse (1980).

vertical line with the extremities corresponding to the minimum and maximum δ-values. Such a pattern could be found where a dominant industrial source emits steadily but alters its feed stocks.

In Figure 2.4, the emission rate of source A is constant but the emission rate of a second source B varies. The δ-values of both sources are different constants. As the emissions from B approach zero, the isotopic composition observed at an appropriate site approaches that of source A and coincides with the minimum concentration. As the emission from B increases, the observed concentration increases and the isotopic composition approaches that of source B. Simple algebraic manipulations permit determination of the δ-value of source B. The isotopic balance may be approximated by the expression:

$$C_A \delta_A + C_B \delta_B = C \delta_{obs} \qquad [1]$$

where C_A and C_B are the concentrations due to source A and B, respectively; C is the observed total concentration; δ_A and δ_B are the δ-values of sources A and B; and δ is the measured δ-value at the observation site.

Since $C_B = C - C_A$, equation [1] may be rewritten to give:

$$C_A \delta_A + (C - C_A)\, \delta_B = C \delta \qquad [2]$$

Further rearrangement gives:

$$\frac{C_A (\delta_A - \delta_B)}{C} = \delta - \delta B \qquad [3]$$

Assuming C_A, δ_A, δ_B are fixed, equation [3] can be written as:

$$\delta = \frac{\text{Constant}}{C} + \delta_B \qquad [4]$$

Therefore, a plot of δ versus concentration^{-1} yields a straight line which intercepts the y-axis at the δ-value for source B.

Figure 2.5 illustrates an idealized plot of δ-values and associated concentration data from an observation site typical of a situation in which the emission rate of a source A is constant but its isotopic composition changes, whereas the emission rate of source B is variable but with a fixed isotopic abundance. Note that random observations would give results in the shaded area of Figure 2.8.

Figure 2.6 introduces a further complication where emission rate of source A also varies. The relationship shown in the figure is expected for data obtained at a site located near a source with variable emission rate (source B) in a partially-forested/farming/ranching area (sources A). Both sources would be variable with respect to concentration if the winds transporting emissions to the observation site were not constant. Also, the measured δ-value would vary with the wind direction since different proportions of emissions from the various sources A would reach the sampling site. The δ-value of source B would be constant, assuming the industrial feed stock was isotopically uniform. It is obvious that as emissions from source B increase, the contributions from sources A (heterogeneous background) will be "masked" and the measured total δ-value at the observation site will approach that of source B.

Figure 2.7 illustrates a situation in which two sources, A and B, have variable emission rates but fixed isotopic compositions. Data points for an observation site will fall somewhere in the shaded area. The boundary lines correspond to the δ-values of the sources, while their actual lengths represent the range of concentration attributable to each source. Points falling on either horizontal line would signify that the ambient concentration is due almost solely to the corresponding source.

In Figure 2.8, source B is dominant but a large number of smaller sources of various isotopic composition abound. Since these sources are small, their presence can be noted only when the concentration of B is low. With increasing concentration, the proportion of B increases and the composite δ-value approaches that of source B.

Figure 2.9 illustrates a small source fixed in its emission rate and δ-value, in the midst of several variable sources which differ in their δ-values. At the lowest concentration observed, the δ-value is that of A since it is the sole source. With increasing concentration, the variable sources contribute a greater proportion and the range of δ-values may depart significantly from that of source A (the extremes, if reached, would be the maximum and minimum $\delta^{34}S$ values encountered in nature).

These hypothetical cases can be employed to assess the extent to which different sources contribute sulphur to the enviornment in the vicinity of sour gas processing plants. This is possible because of the relatively large amounts of SO_2 and elemental S dust emitted by such processing plants which typically have $\delta^{34}S$ values ranging from +5 to +30 $^{o}/_{oo}$. Natural sulphur emissions have a much wider $\delta^{34}S$ value range but are usually present in much lower concentrations.

2. THE STUDY AREA

2.1 LOCATION AND SIZE

The samples were gathered at locations within a 20 km radius of the Amerada-Hess flaring installation near Sturgeon Lake (10-29-71-23 W5M), approximately 20 km northwest of Valleyview, Alberta (Figure 3 and Appendix 9.2).

2.2 PHYSIOGRAPHY AND SOILS

The majority of soils in the area are Gray Luvisol and Gray Solonetzic soils developed on glaciolacustrine clay (sometimes called lacustrotill). These soils usually fall within the Donnelly group (Appendex 9.3). The bedrock of the area is composed of Upper Cretaceous dark gray shale deposits and the overlying till or lacustrine deposits produced a gently undulating surface.

2.3 VEGETATION

The native vegetation of the area is dominated by trembling aspen (*Populus tremuloides*) forest, with some open areas of Agropyron stipa grasslands typical of the "Peace River Prairie." There are some locally important conifer-dominated areas (e.g., black spruce, *Picia mariana-Sphagnum* muskeg). Because these areas tended to be localized, they were not studied.

The structural and floristic features of trembling aspen stands are summarized in Appendix 9.4.

The epiphytic lichen flora associated with trembling aspen have been discussed in detail previously (Case 1977).

2.4 HISTORY OF THE AMERADA-HESS FACILITY

The first battery located at 10-29-71-23 W5M began gas production in 1952. In 1954, a second battery at 16-31-71-23 W5M began production. These batteries operated separately until June 1978. From then on, all gas was produced at the central battery at 10-29-71-23 W5M.

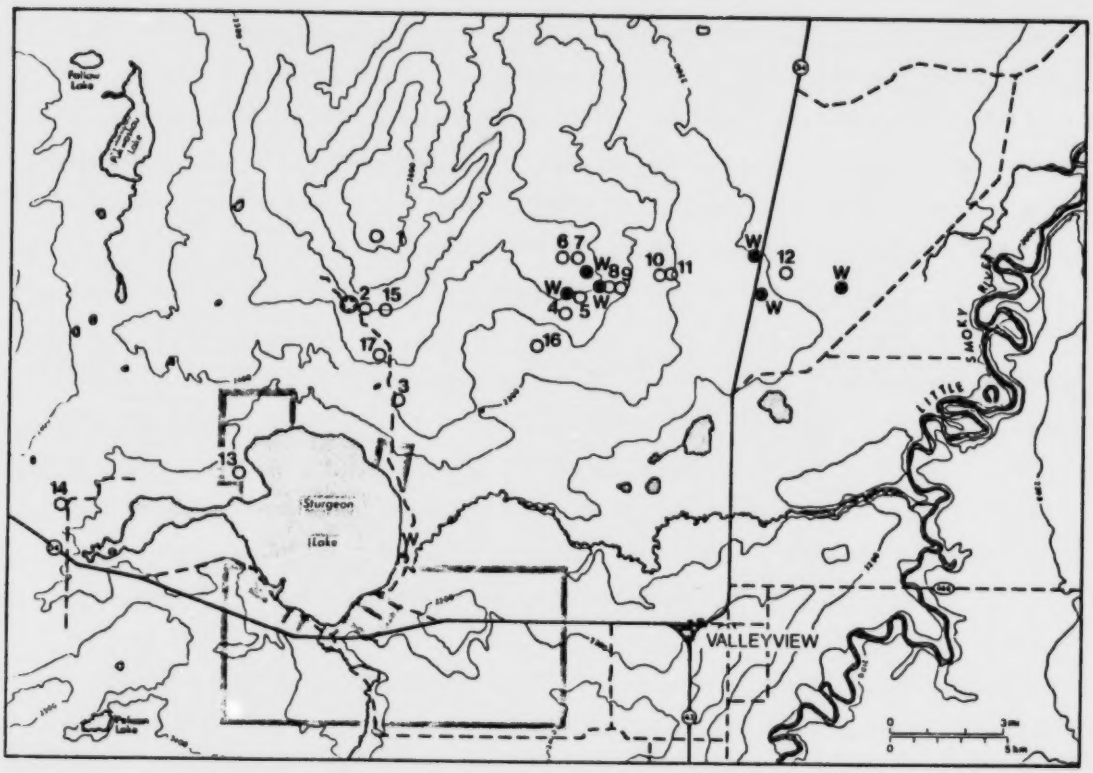

Figure 3. Locations of sampling sites in the Valleyview area. Flare stack is shown by the circled star.

The gas was flared at the central facility until about May 1980, when a line to the Sturgeon Lake South gas plant was completed to conserve and process the gas.

Essentially, all gas produced was flared until May 1980. At each of the batteries, some of the gas was used as lease fuel without sulphur recovery.

The summary information on the gas production and sulphur emissions is presented in Appendix 9.1. From 1952 to 1979, the batteries cumulatively released a total of approximately 53×10^3 t of sulphur into the environment. This compares to the total emissions for less than five years of a larger sour gas plant operation, or the output in a few months of a stack at a major metal sulphide refinery (e.g., Inco "super-stack" at Sudbury, Ontario; Mt. Isa, Australia).

3. MATERIALS AND METHODS

3.1 SAMPLING OF PRODUCTION WELL GASES

Sulphur present in the feed gas is emitted into the atmosphere without any appreciable effect on the $\delta^{34}S$ value. Thus, the determination of the sulphur isotope composition of hydrogen sulphide entering the stack prior to combustion is the first step necessary in tracing the fate of sulphur compounds emitted to the environment. If sulphur released by the flare stack was absorbed by the surrounding environment, over time, the $\delta^{34}S$ values for soil, vegetation, and water should tend to approach those of the emissions. Also, for samples closer to the flare stack, the $\delta^{34}S$ values should increasingly resemble those of the source. This trend will be influenced by topography and meteorological factors such as prevailing winds (especially during growing season) and inversions.

Samples of hydrogen sulphide were collected using the valves located on pig-traps at the flare plant. The sour gas (32% H_2S) was bubbled through a tube containing 1 molar solution of cadmium acetate. The exit gas was then bubbled through a second identical apparatus to trap any sulphide not removed in the first trap. The presence of hydrogen sulphide was revealed by the formation of a bright yellow-orange cadmium sulphide precipitate. For the several hydrogen sulphide samples collected in this manner, no cadmium sulphide was detected in the second trap signifying quantitative recovery.

Subsequent to collection, aliquots of the cadmium sulphide were converted to hydrogen sulphide and reprecipitated as cadmium sulphide. This acid distillation procedure ensured that no interfering organic contaminants were present. The purified cadmium sulphide was then treated with 0.1 N $AgNO_3$ solution to produce the silver sulphide (Ag_2S) necessary for stable isotope relative abundance (SIRA) analysis.

3.2 ATMOSPHERE

The $\delta^{34}S$ values of sulphur in the particulate matter and SO_2 in the atmosphere are a function of their sources. The sulphur dioxide

emitted by the flare stack has a sulphur isotope composition essentially the same as the hydrogen sulphide in the feeder gas.

The objective of the ambient air sampling was to determine the extent to which the sulphur in the air arriving at a series of sampling sites was dependent on flare emissions. Sampling was conducted before and after regular gas recovery was initiated at the Amerada-Hess Installation.

3.2.1 High-Volume (Hi-Vol) Sampling Array

An array of nine high-volume air samplers was deployed at four locations and operated for approximately one week. An electronic switching system controlled the array, turning on or off one of the eight designated samplers when the wind was blowing from the NNE, ENE, ESE, SSE, SSW, WSW, WNW, or NNW. If the wind speed dropped below 2 km/h, the ninth air sampler was selected to sample the sulphur associated with the low wind speed. Chronometers (digital counters) kept track of the number of minutes each sampler was in operation. The sampler array was left in operation until each sampler had run for about 360 min or until any one sampler had operated for a maximum of 2500 min.

3.2.2 Integrated Sampling

Two additional hi-vol air samplers were used to sample continuously. One unit was located on the roof of the Provincial Building in the Town of Valleyview, and the second unit at the Erhard Dallman Farm (14.6 km NNW of Valleyview) where there had been several complaints of sulphurous gas fumigation episodes, especially when the wind was from the general direction of the flare stack.

3.2.3 Sample Collection

The air was pulled through the sampler by a fan powered by a load-compensating electric motor. The air passed through a series of five slotted glass fibre filters, which selectively removed particulate matter in aerodynamic size classes with nominal cutoff points of 7.2, 3.0, 1.5, 0.95, and 0.49 microns. The air was then drawn through a filter

impregnated with a TEA (triethanolamine)-KOH mixture which chemically bound sulphur dioxide.

In the laboratory, the filters with the particulate samples were treated with an $HCl-H_3PO_2$ reduction mixture (Thode et al. 1961) in a distillation apparatus. The generated hydrogen sulphide was trapped as cadmium sulphide and subsequently converted to silver sulphide by the addition of 0.1N silver nitrate. This silver sulphide contained all the sulphur present in the particulate matter collected according to their size class. In some instances where insufficient sulphur was present in one size class of particulate matter, the sample was combined with that from the next size class.

The TEA-KOH filters were washed with de-ionized, double-distilled water and the washings oxidized by the addition of hydrogen peroxide to assure conversion of all sulphur species to sulphate. The sulphate was precipitated as $BaSO_4$ by the addition of hot 0.1N $BaCl_2$. The $BaSO_4$ was treated with a $HCl-HI-H_3PO_2$ reduction mixture to generate H_2S which was converted to Ag_2S as described previously.

3.3 RAIN (BULK WET AND DRYFALL SAMPLES)

Figure 3 shows the sites where bulk samples of wet and dryfall were collected. Samples were collected in large plastic garbage pails.

Samples were filtered and preserved with toluene. Dissolved inorganic sulphate was collected using ion-exchange columns. Thus, $SO_4^=$ in the rainwater plus that dissolved from the dry deposition were analysed. The sulphate was precipitated as $BaSO_4$ by the addition of hot 0.1N $BaCl_2$. The $BaSO_4$ was then converted to Ag_2S as described previously.

3.4 SURFACE WATER

An increase in sulphur content, with a tendency towards the sulphur isotopic composition associated with the atmospheric emissions provides a measure of the input of industrial sulphur to the hydrosphere.

In order to obtain the most representative data possible, and also to allow inter-site comparisons, collection of surface water samples

was largely restricted to dugouts used as sources of drinking water. Water samples (2 L) were collected from several dugouts. Samples were also taken from Sturgeon Lake at several locations. Dissolved sulphate was extracted using ion-exchange columns. The sulphate was precipitated as $BaSO_4$ by the addition of hot 0.1N $BaCl_2$. The $BaSO_4$ was then coverted to Ag_2S as described previously.

The sulphate content of the water samples was determined spectrophotometrically using methylene blue as an indicator.

3.5 SOIL

Sulphur dioxide emissions and particulate sulphate of industrial origin have been implicated in the modification of soil characteristics in many parts of the world. These modifications have principally included changes in pH, reduced buffering capacity, and altered patterns of nutrient cycling (Hutchinson and Havas 1978; Overrein et al. 1980). Decrease in soil pH is of great concern in the study area since the upper horizons are naturally acidic and any additional pH decreases could potentially affect agricultural productivity.

An increase in soil sulphur content accompanied by a decrease in the buffering capacity, and an isotopic shift of the sulphur toward that of the stack gas, indicate the uptake of such emissions.

3.5.1 Soil Sampling

Soil samples were collected from pits at 15 study sites (Figure 3) described by Mr. Len Knapik of Pedology Consultants, Edmonton (Appendix 9.3). Soils were classified according to "The Canadian System of Soil Classification" (Canada Soil Survey Committee 1978). Composite samples of the soil horizon (Ap) were collected from cultivated fields using the procedure traditionally employed in soil quality surveys.

The use of soil pits permitted easier classification and collection of samples from each soil horizon. The depth of each horizon was recorded. The colour of the soil prior to drying was determined by comparison to a Munsell colour chart. Observed macro- and mesoscopic structural features of the horizons were noted along with consistency.

3.5.2 Soil pH

Soil pH was determined in the field using pH sensitive indicator solutions. In the laboratory, soil pH was determined by making a slurry of 25 g of soil and 50 mL of distilled water and measuring the pH using a permeable glass electrode pH meter.

3.5.3 Soil Sulphur Content

Soluble $SO_4^{=}$ from all samples was extracted twice using a 0.1M LiCl solution under ultrasonic agitation. The total sulphur of upper soil horizons was determined using the Parr bomb (all forms of sulphur were oxidized to $SO_4^{=}$).

The sulphate produced by each method was precipitated as $BaSO_4$ and converted to Ag_2S as discussed previously. Sulphur content of the soil fractions was determined gravimetrically by weighing the Ag_2S.

3.5.4 Soil Buffering Capacity

The ability of soil samples to neutralize acidity (expressed in terms of meq H^+) was determined using a modification of the $Ca(OH)_2$ reaction method to determine lime requirement (McKeague 1978). Samples (20 g) of dried, ground soil were weighed into 6 disposable plastic cups. Dilute sulphuric acid (0.1N) was added in quantities of 0, 1, 2, 4, 8, and 12 meq of H^+ to cups 1 to 6. The volume in each cup was brought up to 50 mL by the addition of distilled water. The cups were covered with watch glasses and stirred twice a day for 3 days. The pH of each soil suspension was measured using a permeable glass electrode pH-meter. The pH was then plotted against the meq of H^+ added to each soil sample.

3.6 VEGETATION

Figure 3 shows the location of the vegetation sampling sites in the study area. Attempts were made to obtain crop samples from all sites on cultivated land. In adjacent uncultivated sites, free of obvious man-made disturbance, samples of natural vegetation were collected in July 1980. About 1 kg of trembling aspen (*Populus tremuloides*) was collected

from several different trees so as to produce a composite sample. About 50 g of the tree-dwelling lichens (*Parmelia sulcata*) and/or *Hypogymnia physodes* were collected if possible. Absence of lichens at Sites 1 and 2 precluded their collection for analysis. Where possible, samples of ground dwelling lichens and mosses were collected for comparative purposes. Some sites were re-sampled in September 1980.

3.6.1 Sulphur Extraction from Vegetation

The fresh plant material was packaged into self-sealing plastic bags in the field, labelled, and then refrigerated to minimize sulphur conversion during transport to the laboratory. In the laboratory, the plant material was dried in a reduced air pressure oven at 80°C for 24 h. The samples were then ground to a very fine consistency using a Wylie mill equipped with a #30 mesh screen. Soluble sulphur was extracted from pre-weighed subsamples with hot 0.1N LiCl. The sulphate resulting in each situation was precipitated as $BaSO_4$ by the addition of hot 0.1M $BaCl_2$. The $BaSO_4$ was then quantitatively converted to Ag_2S as discussed earlier. The sulphur content was determined gravimetrically by weighing the Ag_2S recovered.

3.7 FERTILIZER

In order to take into account sources of sulphur in plants and soil, other than the precipitation and pollution emissions, samples of the most commonly used fertilizers (including ammonium nitrate prills) were obtained from the local bulk distributors. Sulphur in each sample was quantitatively converted to $SO_4^=$ by chemical oxidation. The $SO_4^=$ was precipitated as $BaSO_4$ which was, in turn, converted to CdS through purification distillation. This was converted to Ag_2S as discussed previously. The sulphur content of the fertilizers was determined gravimetrically by weighing oven-dried Ag_2S or $BaSO_4$.

3.8 SIRA (STABLE ISOTOPE RELATIVE ABUNDANCE) ANALYSIS

In order to determine the abundances of ^{34}S and ^{32}S in a sample, relative to a standard, the sulphur in the sample of interest

must be converted to SO_2 for introduction into the mass spectrometer (some laboratories use SF_6).

3.8.1 Sulphur Dioxide Preparation

The prepared Ag_2S (up to 20 mg) was thoroughly mixed (1:4 by wt) with Cu_2O, and packed into a 0.5 cm x 3 cm quartz tube. This tube was inserted into the SO_2 preparation line which was then evacuated. After 10 min evacuation, the valve to the vacuum line was closed and the quartz tube containing the Ag_2S-Cu_2O moved by a magnetic pushrod into a furnace maintained at 900°C. Sulphur dioxide generated from the thermochemical reaction was frozen in liquid nitrogen and pumped to remove O_2. Minute quantities of H_2O and CO_2 are also produced in these conversions. The H_2O was removed by passing the gases through a trap cooled by a dry ice-acetone slush, while CO_2, because of its higher vapour pressure, was removed by a vacuum distillation from a trap cooled by a n-pentane slush (the pentane was cooled down to its solidification point by adding liquid nitrogen). After these procedures, the SO_2 was ready for isotopic analysis.

3.8.2 Mass Spectrometry

The SO_2 preparation line was attached directly to the mass spectrometer to avoid the expenditures of time and costs of the gas breakseal tubes generally used in other laboratories. The SO_2 is introduced through a magnetic valve system which alternately switches between a reference SO_2 sample and the one which has just been prepared. The mass spectrometer has been built around a Micromass 602 analyser. Ion currents of mass 64 and 66 were digitized and passed to an AIM65 micro-computer which calculated the $\delta^{34}S$ value after corrections were made for oxygen isotope composition at mass 66 ($^{32}S^{16}O^{18}O$) and ($^{34}S^{16}O_2$).

4. RESULTS AND DISCUSSION

4.1 PRODUCTION WELL GASES

The mean $\delta^{34}S$ of H_2S sampled at the base of the emission stack (i.e., prior to combustion) was 17.6 °/oo, based on six separate measurements (16.4, 16.7, 16.9, 17.2, 19.0, and 19.3 °/oo). This $\delta^{34}S$ value is typical for sour gas found in Alberta (Krouse 1977a, 1979).

4.2 ATMOSPHERE

Concentration and $\delta^{34}S$ values for atmospheric SO_2 and particulates are given in Appendices 9.5, Tables 5 to 12, and Figures 4 to 12. Sampling was carried out using the wind directionally controlled high volume sampling array as well as with an individual sampler running continuously.

In interpreting data from the array, it must be remembered that the wind directions are those at 3 m above ground level. Thus, it is risky to use the polar plots for identifying sources since winds aloft generally are different.

In Figure 4, it is seen that the concentration of particulate sulphur in November (after shutdown of the flare) was not noticeably reduced from that observed during 1980 May 27 to June 07, at the Dallman Farm, but the directional dependence is significantly different, with higher concentrations identified with the WSW in early summer and the SSE in November. In Figure 5, the associated $\delta^{34}S$ data are presented. It is noted that the $\delta^{34}S$ values are much lower in November in all sectors, with the higher values corresponding to the higher concentrations from the south, as seen in Figure 4.

The data presented in Figure 6 show that the SO_2 concentrations were markedly reduced in November compared to those observed during May to June. The November concentrations were distinctly low and they possibly represent reduced sampler trapping efficiency due to low temperatures. One notes, however, that in November the SO_2 concentrations were highest with southerly winds. This is consistent with the patterns observed for particulates (Figure 4). The associated $\delta^{34}S$ data shown in Figure 7

DALLMAN FARM

PARTICULATES

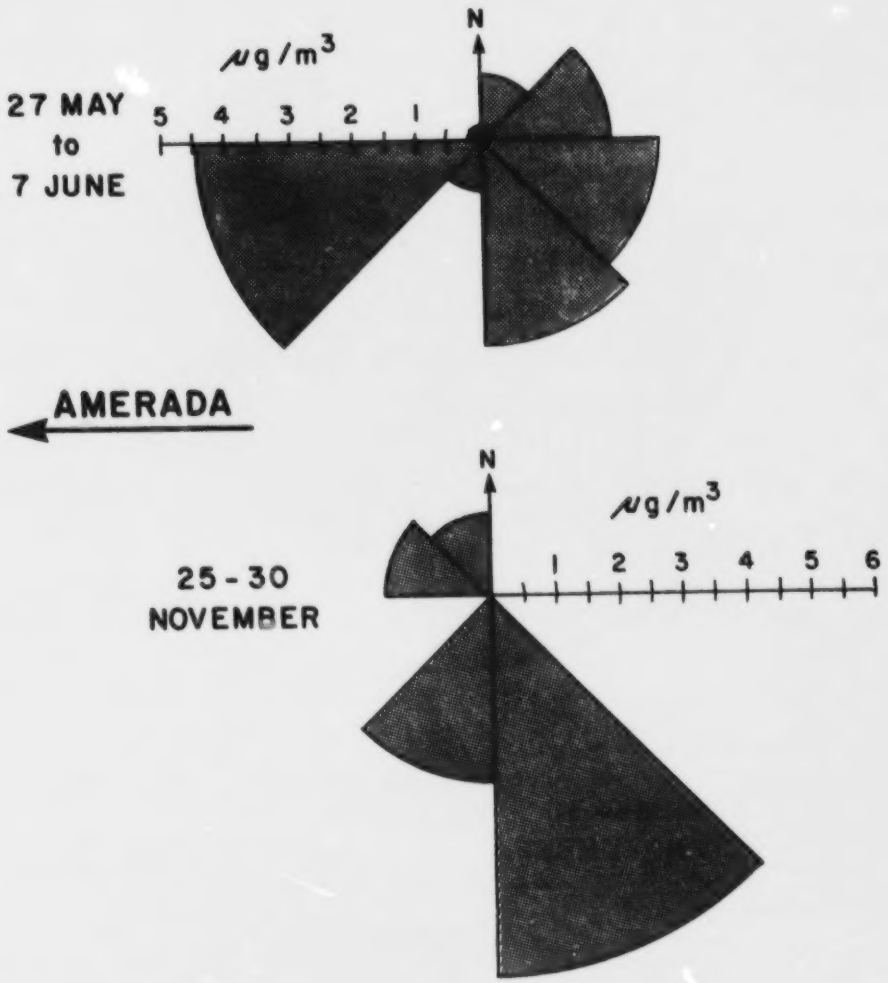

Figure 4. Concentrations of particulates from the high volume sampling array, Dallman Farm. Whereas the higher concentrations were identified with the winds from WSW direction in early summer, they originated from the SSE in November.

DALLMAN FARM

PARTICULATES

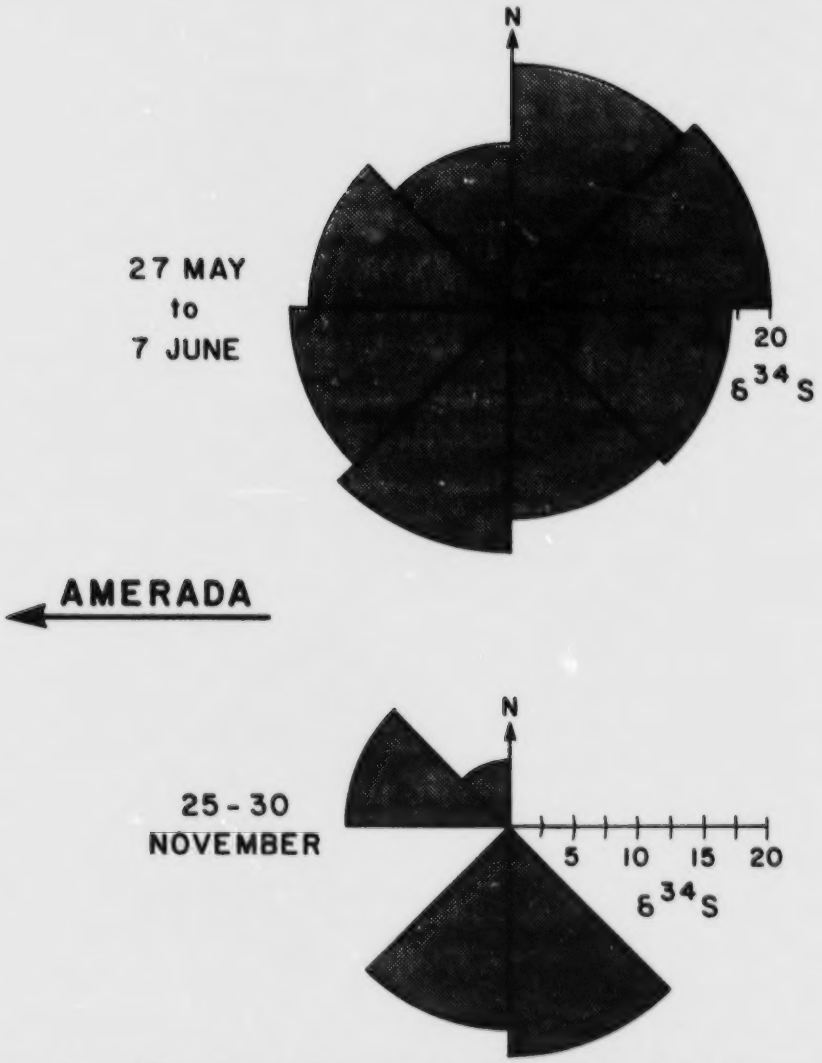

Figure 5. $\delta^{34}S$ values of particulates from the high volume sampling array, Dallman Farm. Note that the $\delta^{34}S$ values in November were lower in all sectors than earlier in the year before flaring ceased. The higher $\delta^{34}S$ values for southerly winds during November correspond to the higher concentrations noted in Figure 4.

DALLMAN FARM

SO_2

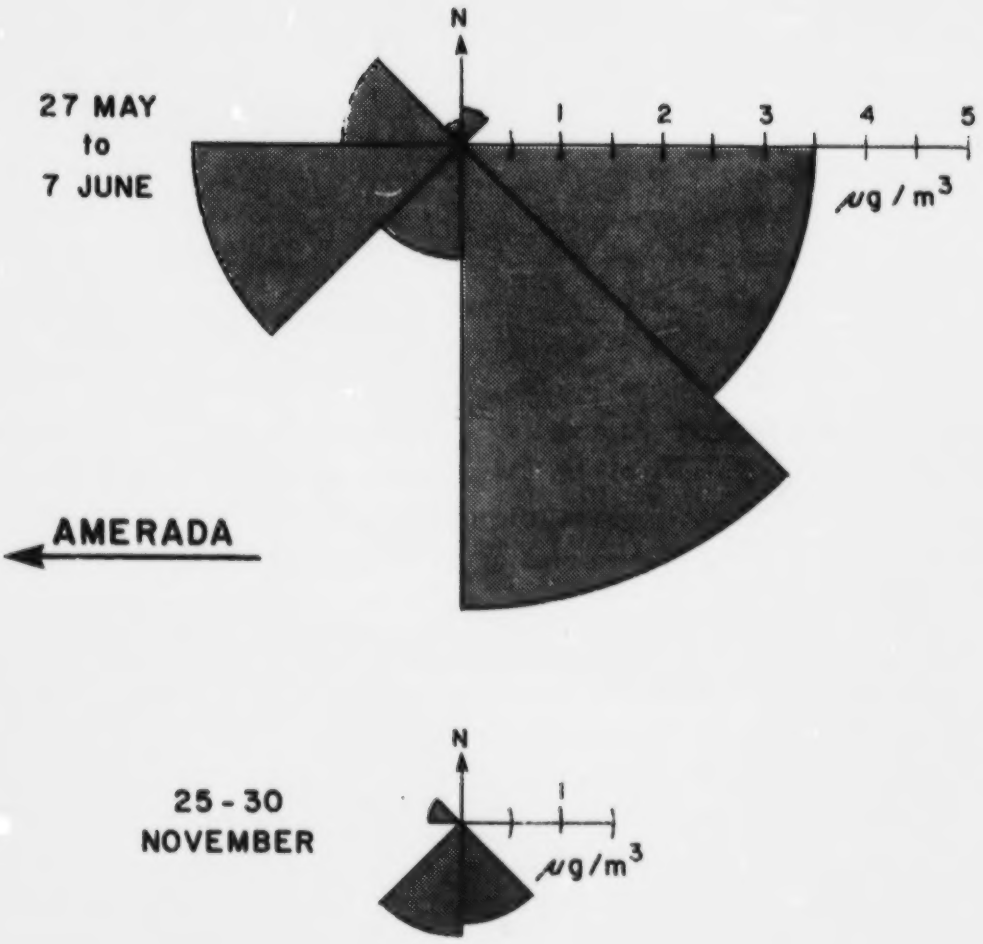

Figure 6. Concentrations of SO_2 from the high volume sampling array, Dallman Farm.[2] Note distinctly lower concentrations in November as compared to the earlier period when the flare was still in operation.

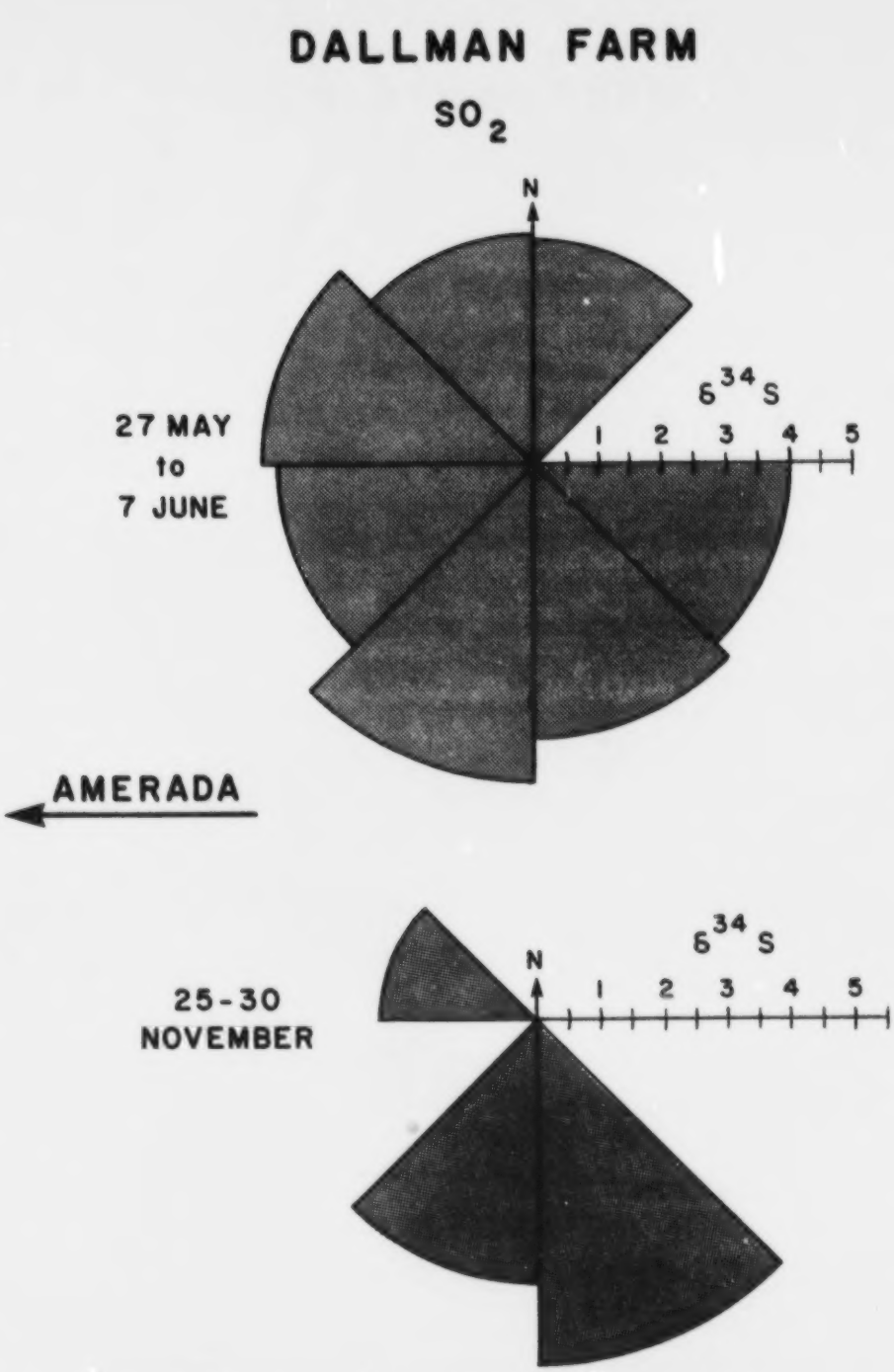

Figure 7. $\delta^{34}S$ values of SO_2 from high volume sampling array, Dallman Farm. Lower $\delta^{34}S$ values were found in November with the exception of the winds from the SSE direction. Compare these data to those for SO_2 concentrations (Figure 6) and particulate matter (Figures 4 and 5).

reveal lower values in November with the maximum value again associated with southerly winds (i.e., high SO_2 concentrations).

Figure 8 summarizes the data on the concentrations of particulate matter and SO_2 and their respective $\delta^{34}S$ values at the Halibisky Farm during November 09 to 19. The $\delta^{34}S$ pattern for SO_2 is very similar to that for particulates, despite significant differences in their concentration patterns. The consistency of the $\delta^{34}S$ values around +8 $^{o}/oo$ suggests a common non-industrial source for the SO_2 and particulates.

Figure 9 presents SO_2 concentrations and $\delta^{34}S$ values at the Gourlay Farm, 1980 December 08 to 12. Comparison of these data with those presented in Figure 8 shows a relatively large sulphur contribution from the general direction of the Amerada plant site in both situations. These high SO_2 concentrations also had similar $\delta^{34}S$ values (near +6 $^{o}/oo$), again suggesting a non-industrial source.

The data from the high-volume sampler array attest to differences in concentrations and $\delta^{34}S$ values with the differences in the wind directions. These data, however, are difficult to interpret precisely without the extensive, supporting meteorological data necessary to document the effect of atmospheric turbulence and diffusion upon ground level concentrations.

Data obtained from continuous high volume sampling are presented in Appendix 9.5, Tables 11 and 12. From mid-June to mid-July, the $\delta^{34}S$ values of SO_2 and associated particulate matter were never lower than +12 $^{o}/oo$, with the majority of values falling between +15 and +20 $^{o}/oo$. In Figures 10 and 11, $\delta^{34}S$ data from the continuous sampler at the Dallman Farm are plotted against SO_2 and particulate sulphur concentrations, respectively. It appears from the limited data that at low concentrations there is considerable variability in $\delta^{34}S$, whereas at higher concentrations, the $\delta^{34}S$ value is much less variable and near +18 $^{o}/oo$, the value associated with the flaring operations active during the sampling period. These data are indicative of the hypothetical model of Figure 2.8 and are suggestive of a dominant source with a $\delta^{34}S$ value near +18 $^{o}/oo$ surrounded by minor sources varying in $\delta^{34}S$ value from less than +12 $^{o}/oo$ to greater than +22 $^{o}/oo$.

HALIBISKY FARM

9 - 19 NOVEMBER

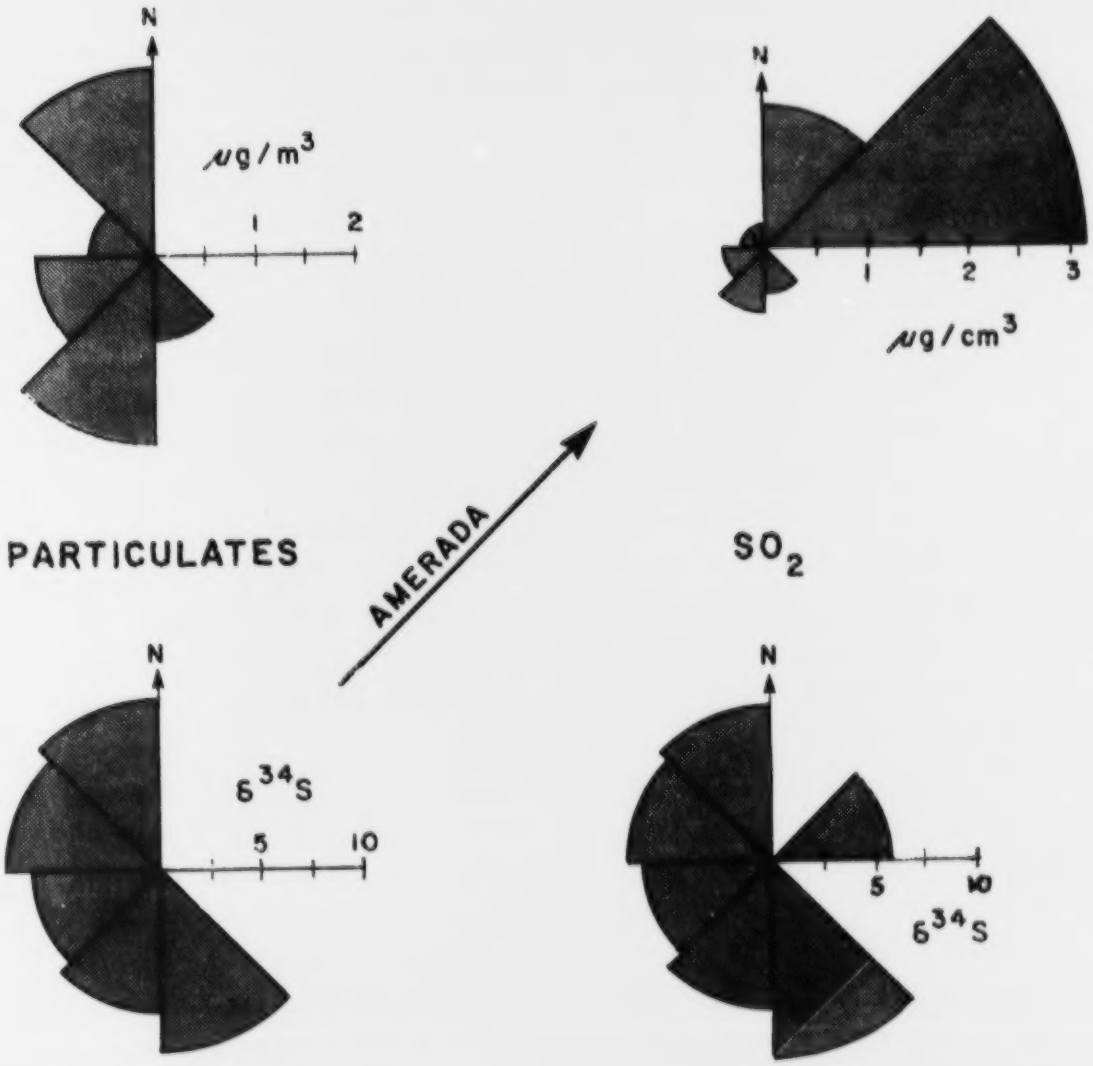

Figure 8. $\delta^{34}S$ values and concentrations of particulates and SO_2 from the high volume sampling array, Halibisky Farm, 1980 November 09 to 19. Note that the $\delta^{34}S$ pattern is similar for SO_2 and particulates despite significant differences in their concentration patterns. A non-industrial origin is suggested by the uniform $\delta^{34}S$ values.

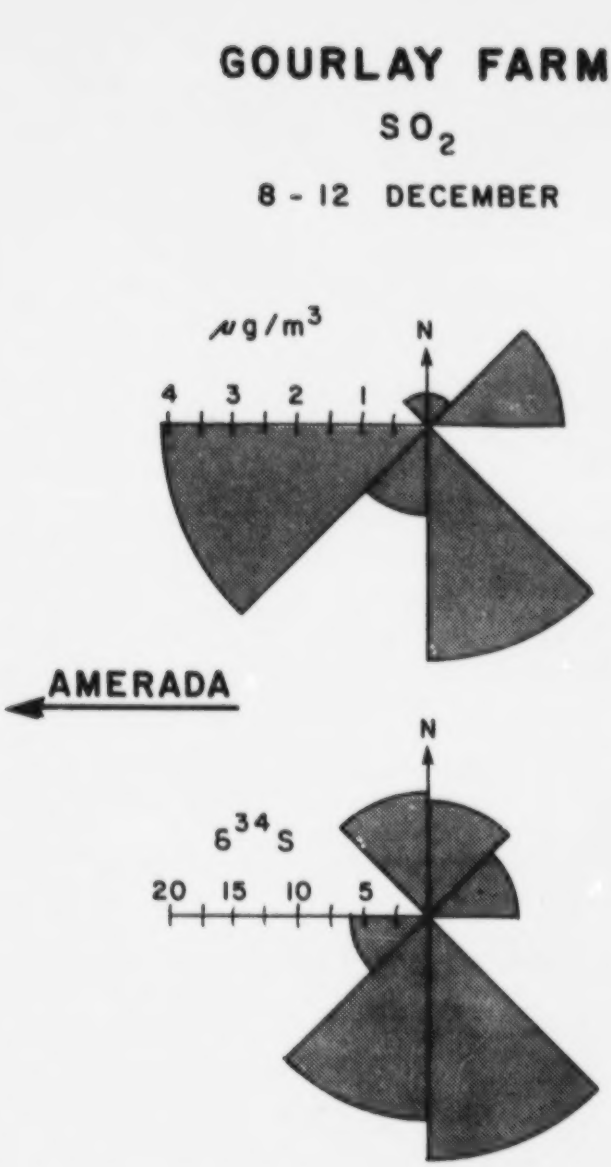

Figure 9. $\delta^{34}S$ values and concentrations of SO_2 from the high volume sampling array, Gourlay Farm, 1980 December 08 to 12. Comparison with the data from the Halibisky Farm, 1980 November 09 to 19 shows a number of similarities including high SO_2 concentrations from the general direction of Amerada, where operations have ceased. In both, the $\delta^{34}S$ value is near $+6^{0}/oo$ suggesting a non-industrial sulphur source.

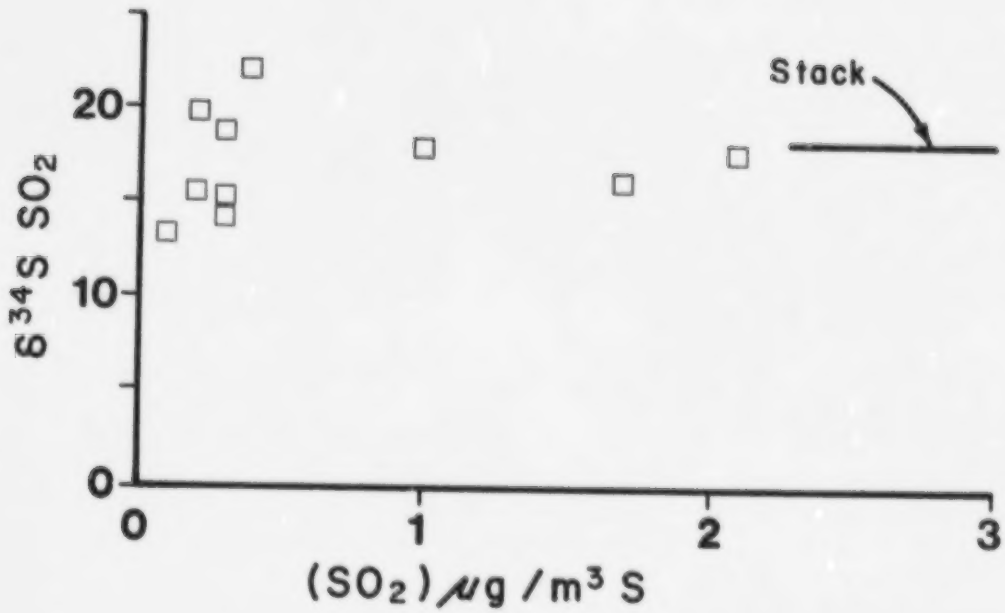

Figure 10. $\delta^{34}S$ vs. concentration of SO_2, continuous high volume sampling, Dallman Farm, mid-June to mid-July 1980. Note that at high concentrations of SO_2, the $\delta^{34}S$ values are close to that of the average stack $\delta^{34}S$ value. (See Figure 2.8).

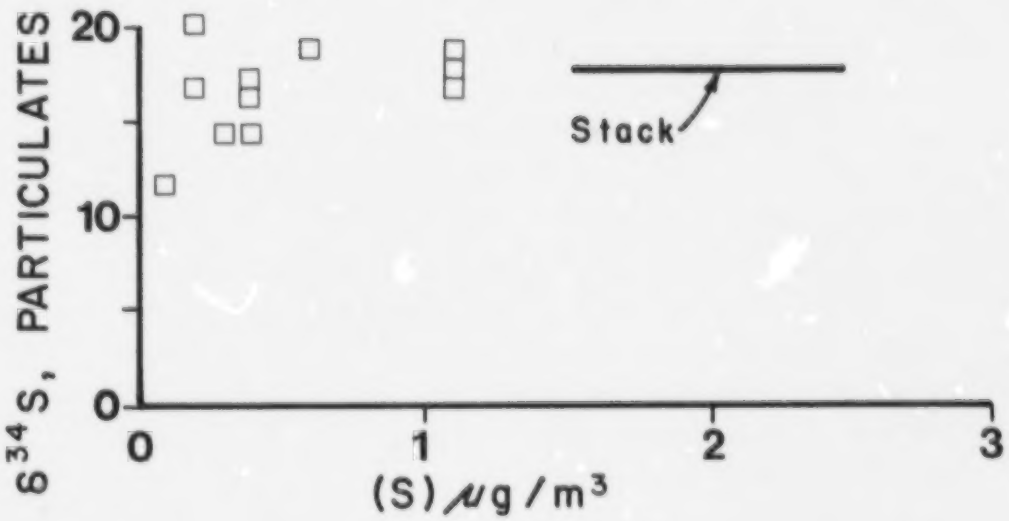

Figure 11. $\delta^{34}S$ vs. concentrations of particulate sulphur, continuous high volume sampling, Dallman Farm, mid-June to mid-July 1980. As with SO_2, the $\delta^{34}S$ values are close to that of the stack for high particulate sulphur concentrations. (See Figure 2.8).

In Figure 12, $\delta^{34}S$ values for particulates are plotted against those for associated SO_2. The figure includes data from the directional as well as individual continuous samplers. In general, the $\delta^{34}S$ values for both particulates and SO_2 decreased after the Amerada flaring ceased. However, there were two anomalous values (Figure 12) for samples collected during the post-shutdown phase. It is not possible to explain the anomaly at this time.

4.3 RAIN

The summer of 1980, unfortunately, was a very dry period and it was difficult to collect sufficient volumes of rain water for analyses. In order to obtain enough sample volume, a large-diameter open container was constantly exposed to the ambient atmosphere. This resulted in the collection of sulphur compounds and other atmospheric constituents deposited both by wet and dryfall. The pH of the collected water, therefore, does not reflect the values for specifically wet precipitation and was not considered useful.

As seen in Figure 13 and Appendix 9.6, while the measured sulphur concentrations are not very high, they still represent inflated values due to the evaporative loss of water in the samples and the presence of dissolved dryfall. The range of $\delta^{34}S$ values of $SO_4^=$ overlaps the $\delta^{34}S$ value of the gas plant emissions. On a quantitative basis, the results presented in Figure 13 can be interpreted as follows. There is a source with a $\delta^{34}S$ value of about +22 $^{o}/_{oo}$ or higher. If the Amerada plant emissions were the only other source, then the $\delta^{34}S$ value should not come below that of the stack (+17 $^{o}/_{oo}$). Therefore, the trend observed at S concentrations below 1 ppm suggests a third source with a $\delta^{34}S$ value near 0 $^{o}/_{oo}$ or lower. A possible third source is wind-blown dust. At the highest concentrations, $\delta^{34}S$ values near those of the industrial input dominated but were slightly lower than the stack emissions, presumably because of the isotopically-light sulphur from the third

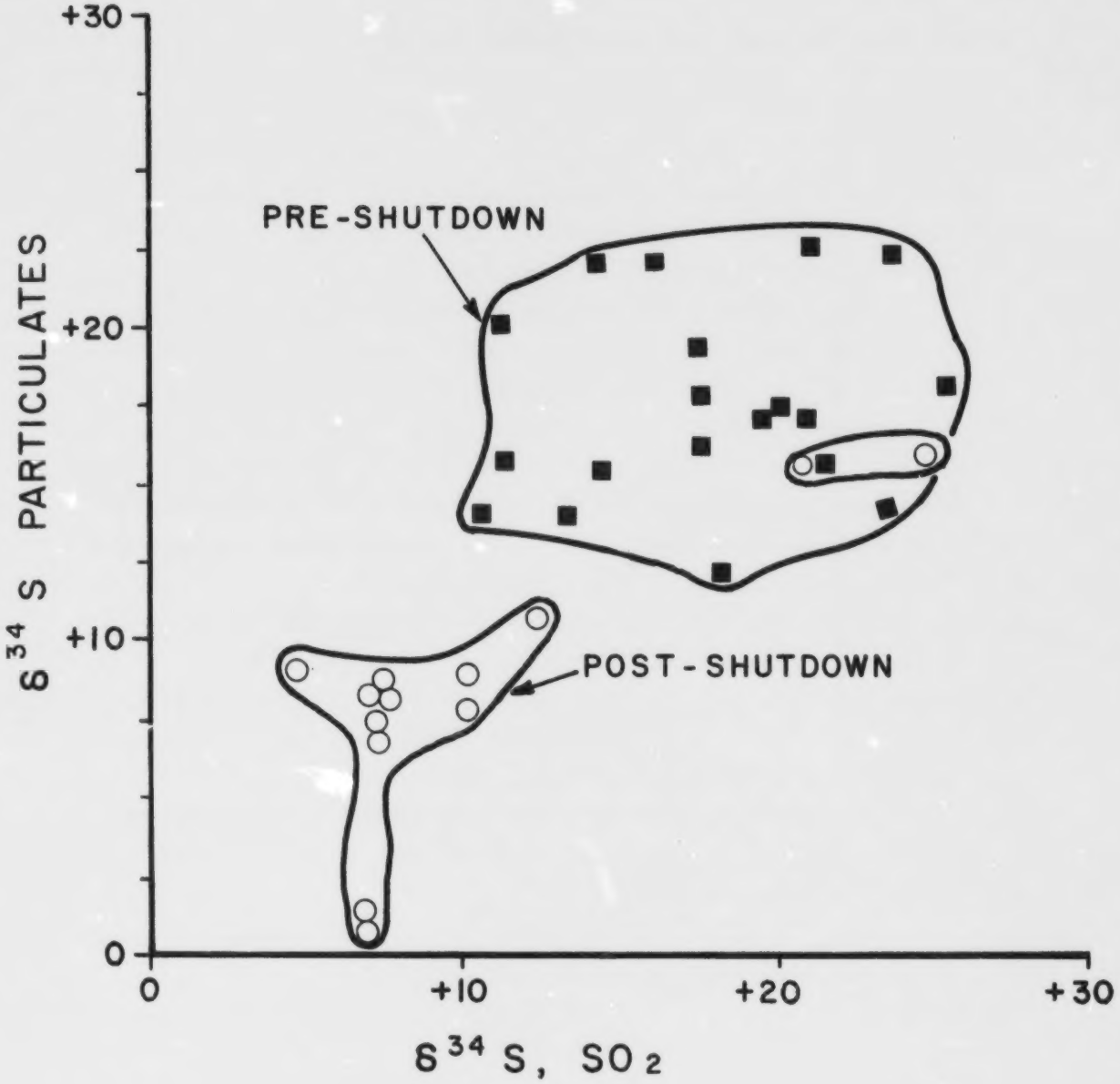

Figure 12. $\delta^{34}S$ values for particulates vs. $\delta^{34}S$ for SO_2. Note that after the Amerada flaring operation was shut down, the $\delta^{34}S$ values of both SO_2 and particulates generally decreased.

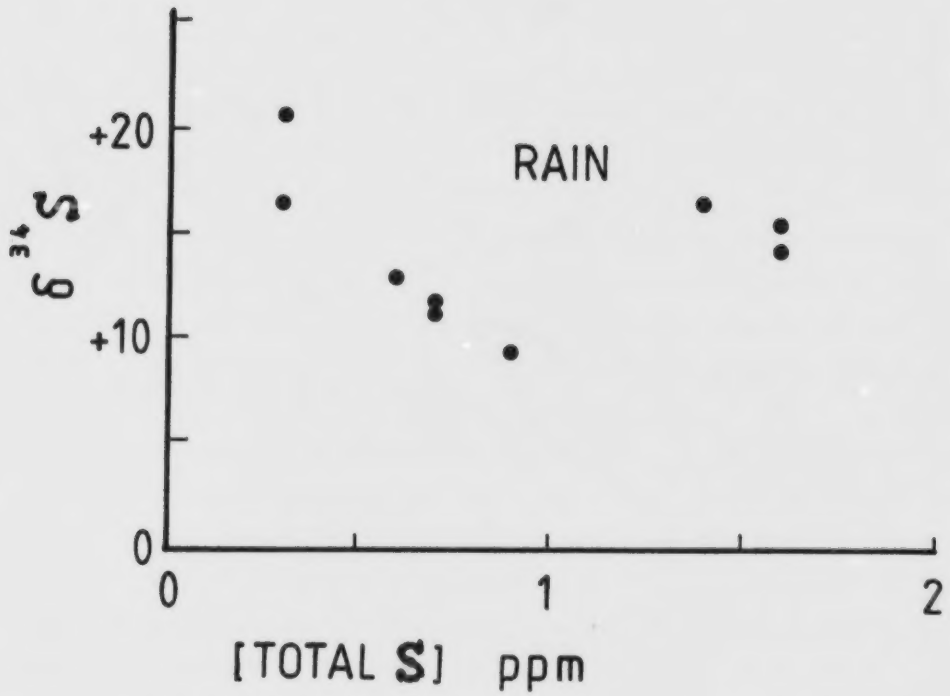

Figure 13. $\delta^{34}S$ vs. concentration of total sulphur in combined wet and dryfall samples. There would appear to be one source with a $\delta^{34}S$ value near $+22^{o}/oo$ which is evident at low S-concentrations. If the stack emissions were the only other source, the $\delta^{34}S$ values should not be lower than $+17^{o}/oo$. Therefore, a third source is indicated with a $\delta^{34}S$ value near that of the emissions.

source. In this context, the limitation of the sample size (n) should be considered.

4.4 SURFACE WATER

Data for surface water samples are presented in Appendix 9.7 and Figure 14. With the exception of the dugouts at sites 12 and 16 (17.7 and 7.6 km E of the stack, respectively) and natural ponds at sites 2 and 15 (0.5 km E and 1.4 km SE of the stack, respectively), samples had $SO_4^=$ concentrations less than 10 ppm. With the exception of the dugout at site 16 and the ponds at sites 2 and 15, the $\delta^{34}S$ values of the $SO_4^=$ fell in the range about -10 °/oo. The $\delta^{34}S$ values are plotted against $SO_4^=$ concentrations in Figure 14. There is a basic problem with this type of plot in that the measured $SO_4^=$ concentration depends upon evaporation as well as $SO_4^=$ input. However, the increase in the $\delta^{34}S$ values with an increase in the $SO_4^=$ concentration would appear to be related to industrial contributions. This applies to sites 2, 15, and 16 which are in the primary dispersion area and have significantly higher $\delta^{34}S$ values (i.e., close to that of the emissions) than waters from other sites (Figure 14).

It would seem relevant that the range of -3 to -10 °/oo, where most of the water samples fall, coincides with the range of $\delta^{34}S$ values encountered in deeper soil horizons (see Section 4.5.3).

4.5 SOIL

The soil classification and description are presented in Appendix 9.3.

4.5.1 The pH Values of Soil

With the exception of the C horizon, the soil samples were generally acidic (Appendix 9.3). The pH of the LFH horizon was not recorded because of its high variability. The average pH of the Ahe-Ae horizons was 5.4. The standard error of the mean pH values was less than

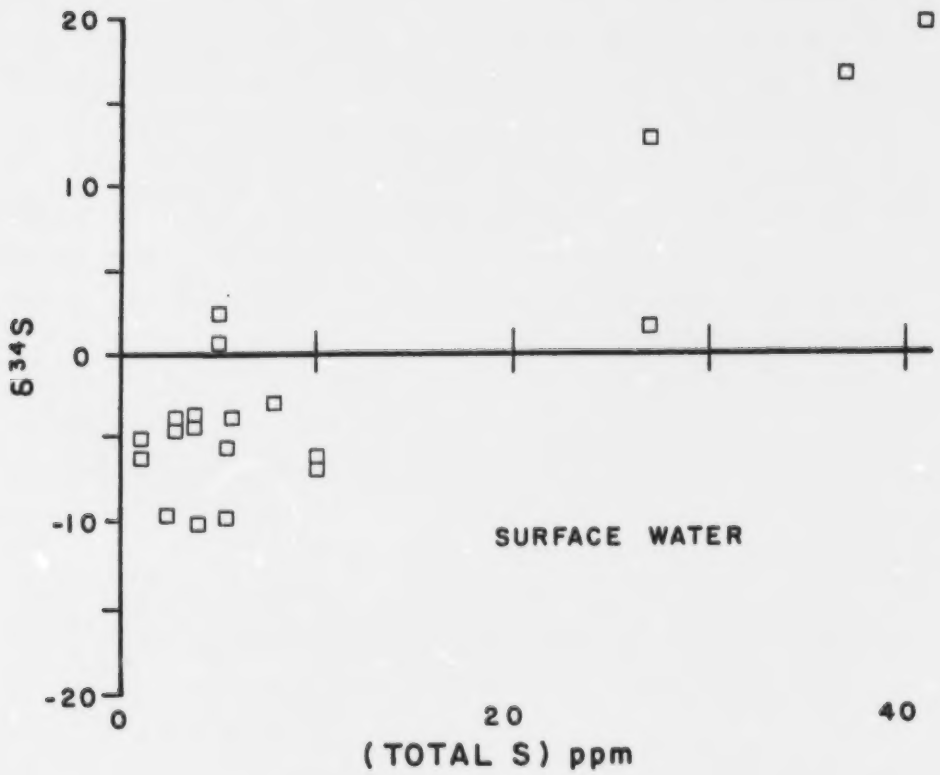

Figure 14. $\delta^{34}S$ vs. concentration of total sulphur in surface waters. $\delta^{34}S$ increases with total sulphur (essentially $SO_4^{=}$) concentration, the higher values being close to that of the flare stack. The majority of $\delta^{34}S$ values are in the range -3 to -10 $^{o}/_{oo}$ which corresponds to the range encountered in deeper soil horizons.

±0.2 indicating that the pH of these horizons is relatively consistent throughout the study area.

The average pH of the Ap (cultivated) horizons was 6.0, with a standard error of less than ±0.1. The average pH of the AB horizon was 5.7 with a standard error of ±0.3. The average pH of the B horizons, excluding the BC layer, was 5.5 with a standard error of less than ±0.1. The average pH of the BC horizon was 6.1 with a standard error of less than ±0.1. Although the trends are not consistent from site to site, the summarized data show that soil pH is a function of acid input to the system and of the degree to which the acids are buffered in the soil. Acids in the soil can originate from atmospheric input, weak organic acids from decomposing organic matter, and CO_2 in the soil solution. Increasing microbial or root activity or a decrease in CO_2 efflux from the soil system (due to decreased aeration) could decrease soil pH. Buffering capacity is usually a function of CEC (cation exchange capacity) and the presence of neutral salts (such as NaCl, Na_2SO_4, and $CaCO_3$). CEC in turn is a function of clay content, mineralogy, and organic matter content and structure.

The C horizons which had the highest pH values, also had relatively high carbonate content, as indicated by vigorous effervescence upon addition of HCl.

The soil pH values were found to be a function of distance from the flare site. They tended to decrease with increasing soluble sulphur concentration in the Ae layer (Figure 15). Data from site 2 were found to be anomalous and additional sites in this area should be sampled before specific conclusions can be reached.

4.5.2 Buffering Capacity

In certain cases, sulphur isotope abundances serve as an effective tool for identifying sources of sulphur in the environment. However, it is an entirely diffferent matter to relate the isotopic data (and in turn sulphur sources) to changes in the environment. Stating it another way, sulphur isotopes can relate sulphur loading of the environment to industrial emissions in certain cases, but the technique

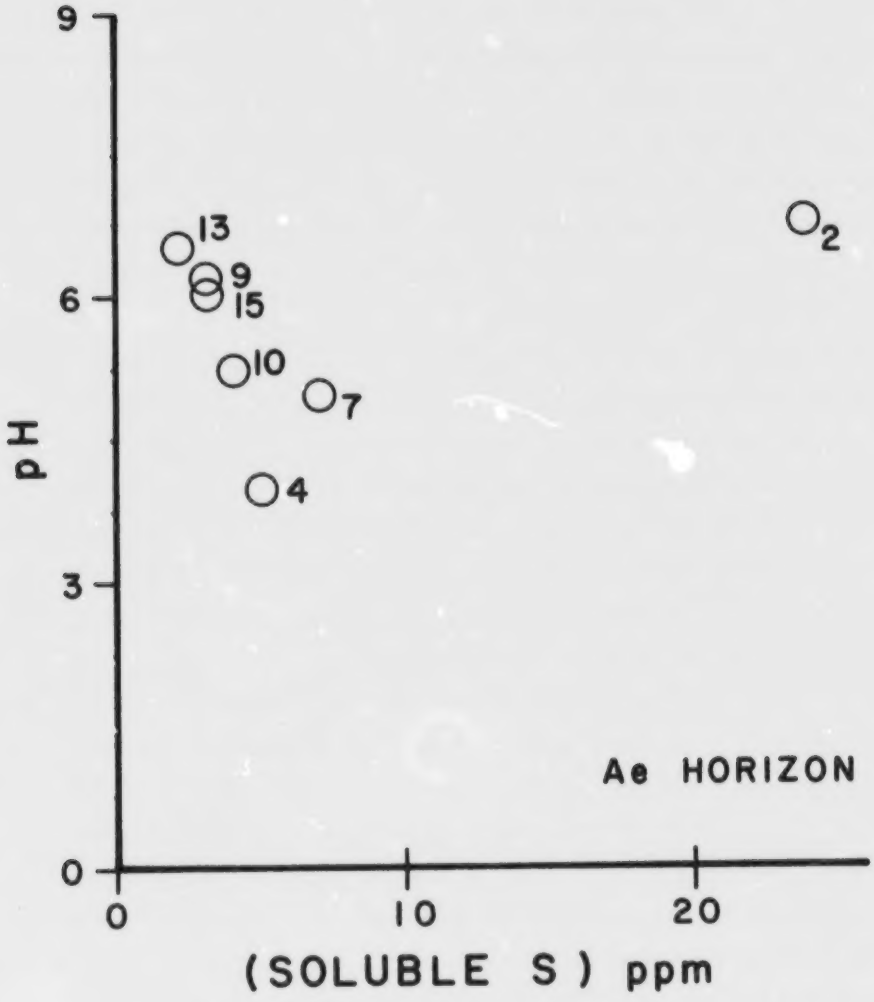

Figure 15. Concentration of soluble sulphur vs. pH in Ae soil horizon. Site 2 appears unusual in that it is closest to the stack, has the highest concentration of soluble sulphur in the AE horizon, yet a near neutral pH suggesting a high buffering capacity.

does not permit evaluation of the consequences of this loading. Techniques and information from other research areas are required for this evaluation. In the case of soils, one chemical criterion is the buffering capacity (the ability of the soil to maintain a relatively constant pH following additions of either acidic or basic solutions). Although not in the initial terms of reference, the buffering capacities to acid addition of a few selected soil samples from the Valleyview area were examined upon later request. The results are presented in Figure 16. Without a thorough organic and inorganic chemical analysis, however, interpretation is somewhat limited.

The variations in the titration curves from site to site were greater than trends associated with soil depth. The BC horizon was found to have slightly higher buffering capability than the overlying horizons, particularly at sites 5 and 6.

The C horizon at all sites maintained a pH above 7, even at the highest H^+ concentration added. One exception was the Ck layer at site 3, where the pH dropped below 6 when more than 2.0 meq H^+/100 g soil were added as H_2SO_4. It is noted that this corresponds to a $SO_4^=$ addition equivalent to 160 ppm S. This is considerably less than the cumulative amount of sulphur added by industrial emissions over the years at the more exposed sites. The 160 ppm S is roughly 10 times the average $SO_4^=$ concentration currently found in the upper horizons of the Valleyview soils and is comparable to the concentrations in the C horizon (Appendix 9.6). This discrepancy arises because sulphur is also removed from the soil by leaching and runoff, as well as by uptake by vegetation. In addition to the problem of estimating inputs and outputs of sulphur, the field situation is not simply one of adding H_2SO_4 to soil. Sulphur is being added in many other forms, including insoluble compounds as inorganic matter. A further complication is that H^+ may be introduced from non-sulphurous sources.

4.5.3 Soil Sulphur Concentrations and $\delta^{34}S$ Values

Soil sulphur content and $\delta^{34}S$ data are presented in Appendix 9.8. The emphasis was placed upon soluble sulphur, since it is the principal fraction available to vegetation.

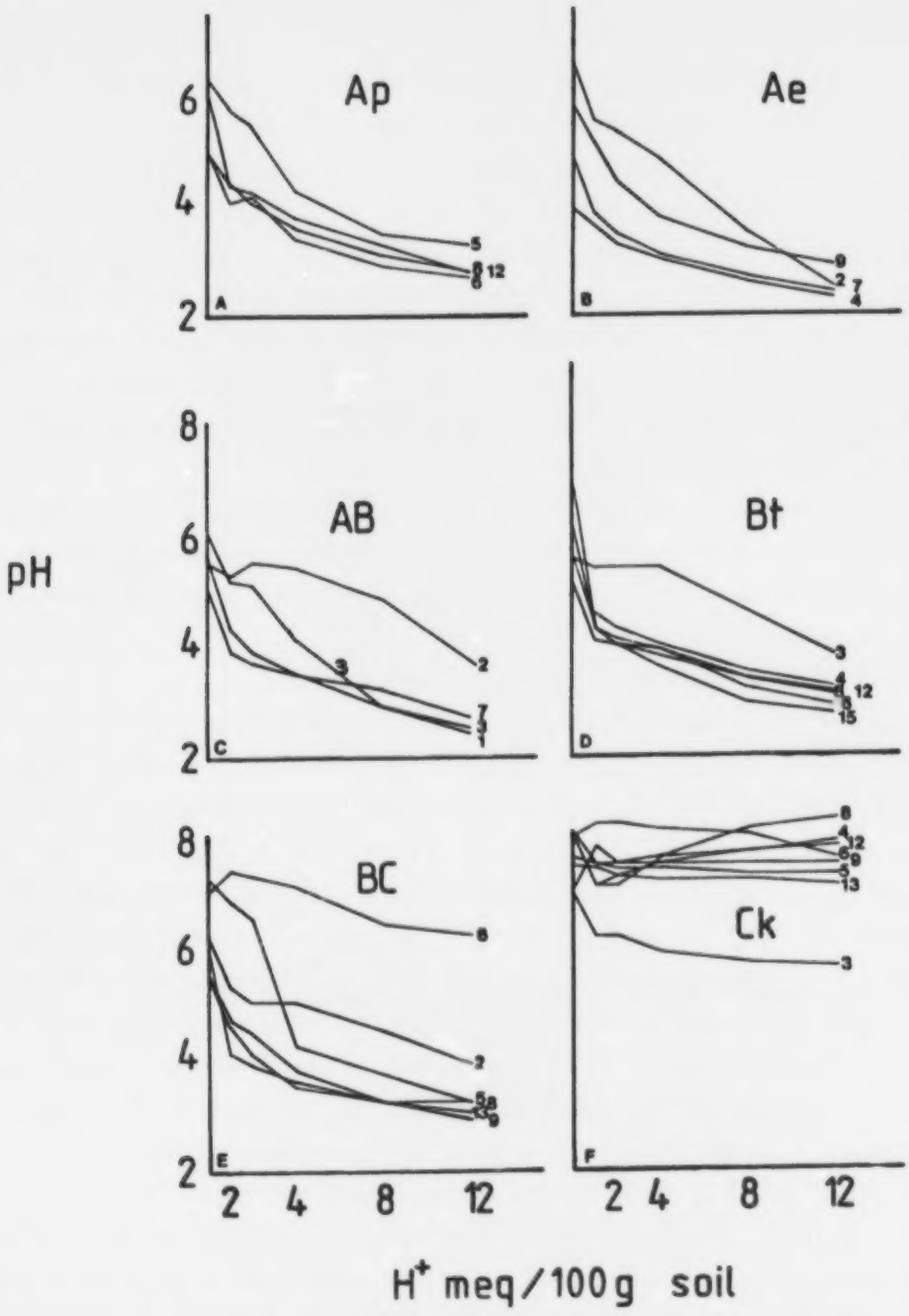

Figure 16. Titration curves illustrating buffering capacity of soils in the Valleyview area. The numbers refer to sites. Sites 2 and 3 are located near the flare stack. Note that with the exception of site 3, the pH is maintained above 7 in the C horizon despite the addition of acid.

In the LFH horizon, the soluble sulphur component (defined as extractable with LiCl solution under ultrasonic agitation) proved to be a small fraction of the total sulphur present. Figure 17 shows that no simple relationship exists between soluble and total sulphur concentrations. However, in lower horizons the soluble and total sulphur concentrations were more comparable. In many locations, the soluble and total sulphur concentrations of the deeper horizons were greater than those of the corresponding LFH layer (Appendix 9.8).

If SO_2 is absorbed by soil solution, one would expect the soluble sulphur concentration in the soil to decrease with distance from the stack. Such a trend is suggested for the Ae horizon in Figure 18. Sites 1 and 14 have permeable sandy parent material which would permit more rapid leaching of soluble compounds.

Whereas sulphur concentration data may elucidate the input and throughput of sulphur compounds in soil horizons, sulphur isotope abundances are more useful. In the LFH horizons, all $\delta^{34}S$ values for soluble sulphur were positive and generally increased with the S concentration (Figure 19), albeit with considerable variability.

In the Ae horizon, the $\delta^{34}S$ values for soluble sulphur are generally lower than in LFH, with a slightly negative value at site 4. This site is known to have abundant salt crystals in the C horizon (Appendix 9.3). The $\delta^{34}S$ values tend to increase with S concentration, with sites 1 and 15 displaying deviations similar to those noted in the LFH horizons (Figure 20).

In the Bt horizon, concentrations of soluble sulphur greater than 10 ppm are associated with $\delta^{34}S$ values between -5 $^{o}/_{oo}$ and -12$^{o}/_{oo}$ (Figure 21). Site 4 with its high salt content in the C layer has the largest S concentration and a $\delta^{34}S$ value of -10.6$^{o}/_{oo}$. The negative $\delta^{34}S$ values are diagnostic of the subsurface sulphur sources which dominate the BC and C horizons (Figures 22 and 23). The $\delta^{34}S$ value of +5$^{o}/_{oo}$ for the BC horizon at site 6 is atypical (Figure 22) and is more characteristic of the values in the upper horizon. This may reflect soil turnover during cultivation.

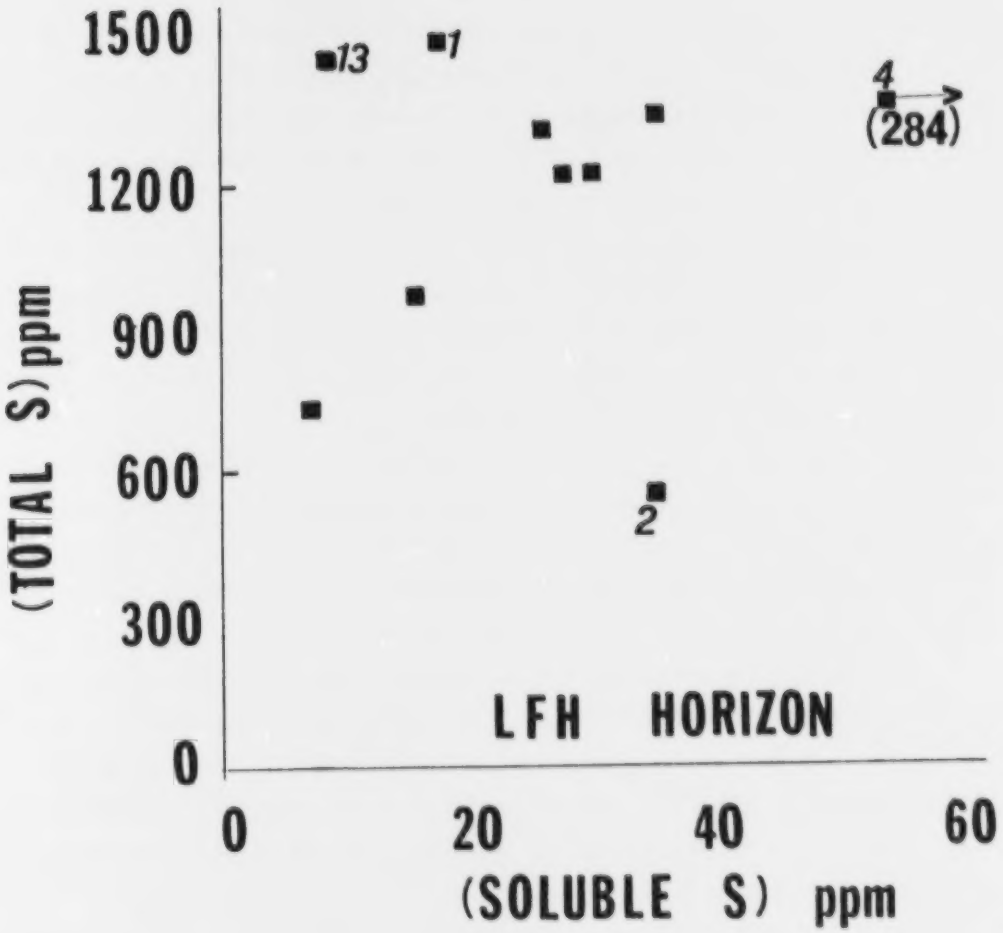

Figure 17. Concentrations of total sulphur vs. that of soluble sulphur in the LFH horizon. Site 2 appears anomalous (see also Figure 15), with its low total S content despite its proximity to the flare.

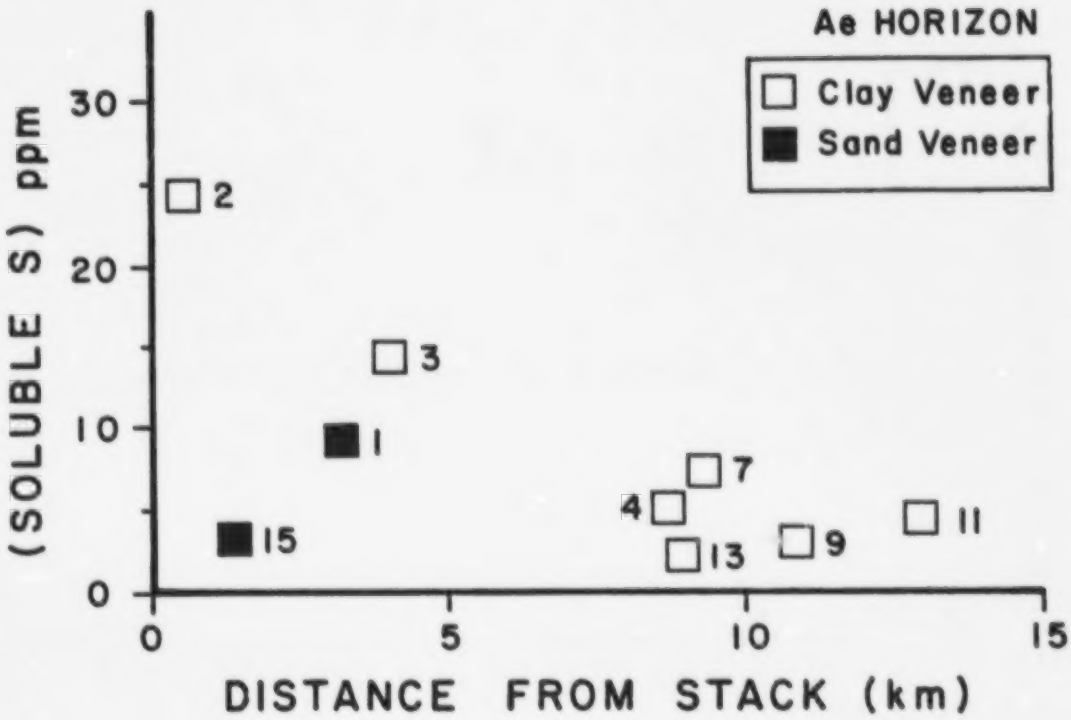

Figure 18. Concentration of soluble sulphur in Ae horizon vs. distance from the stack.

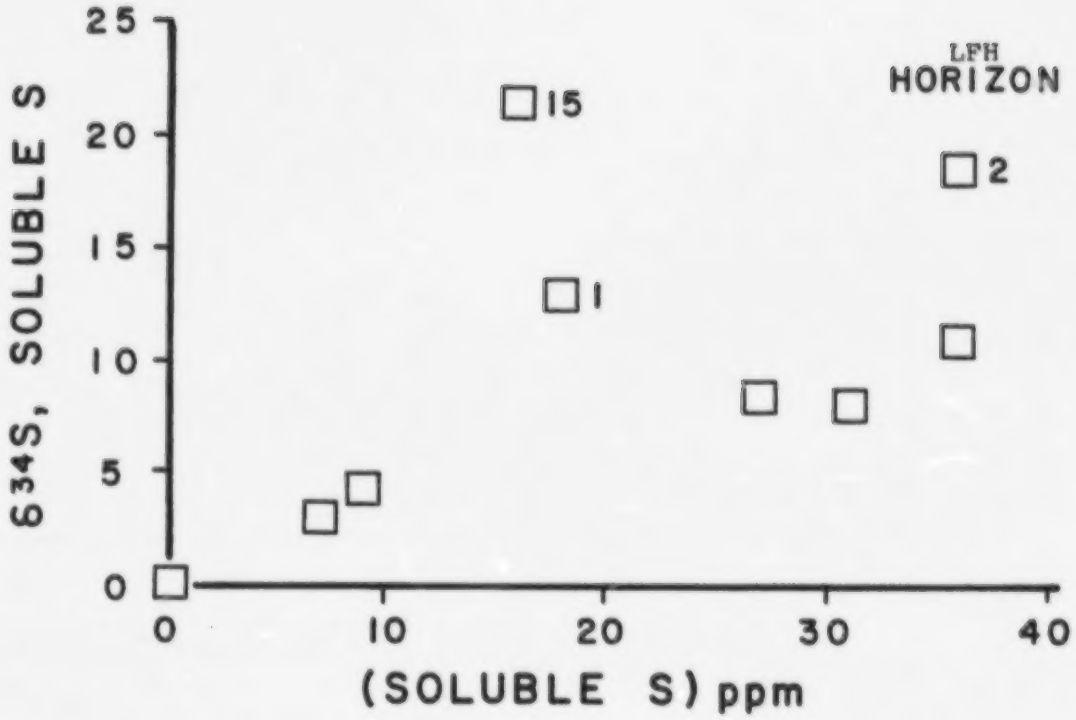

Figure 19. $\delta^{34}S$ vs. concentration of soluble sulphur in LFH horizon. See discussion regarding sites 1, 2, and 15 in Figure 20.

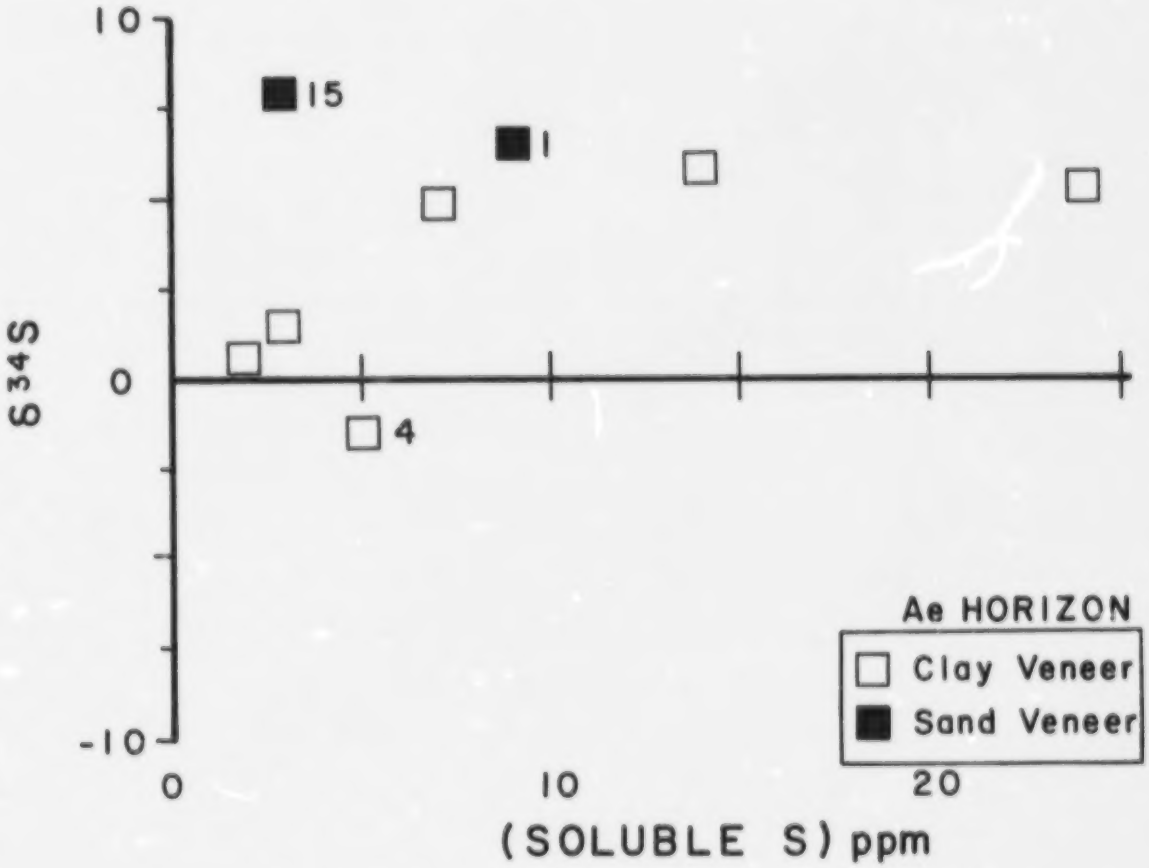

Figure 20. $\delta^{34}S$ vs. concentration of soluble sulphur in Ae horizon. Sites 1 and 15 have lower S-concentrations than expected from their proximity to the stack and this would seem related to their sandy parent material. The lowest $\delta^{34}S$ value at site 4 probably relates to salt crystals found in deeper horizons.

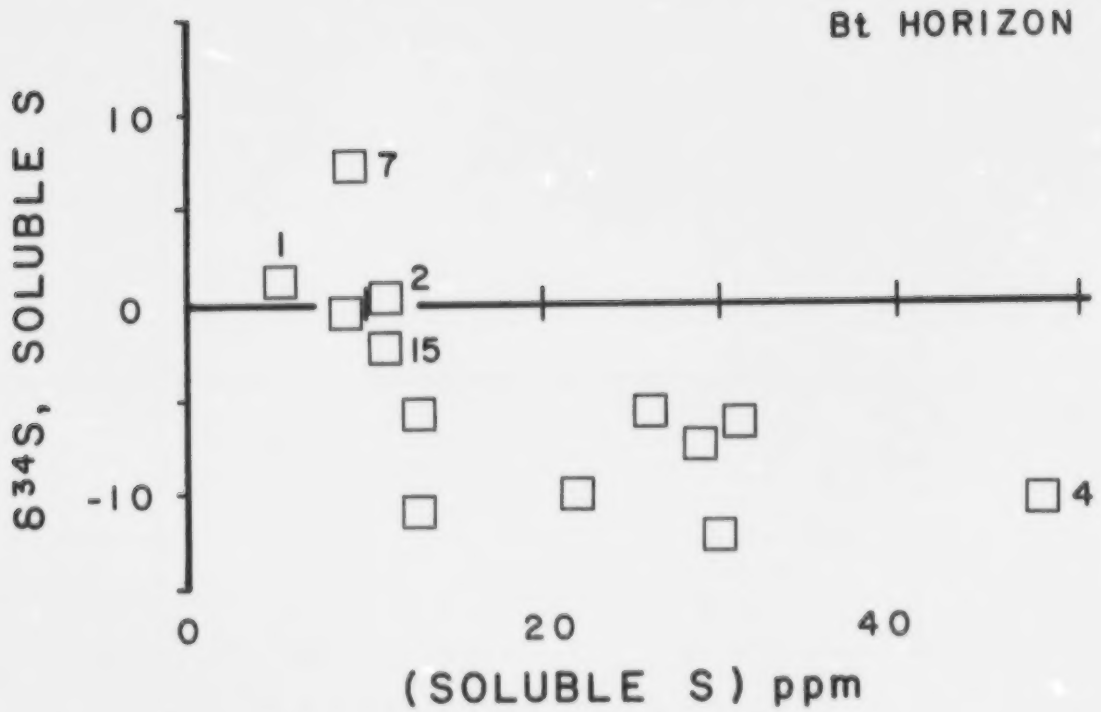

Figure 21. $\delta^{34}S$ vs. concentration of soluble sulphur in the Bt horizon. Note the trend of decreasing $\delta^{34}S$ with increasing concentration, diagnostic of a subsurface source with a $\delta^{34}S$ value of about -12 $^{o}/_{oo}$. Site 4 with the highest concentration has salt crystals in the C horizon.

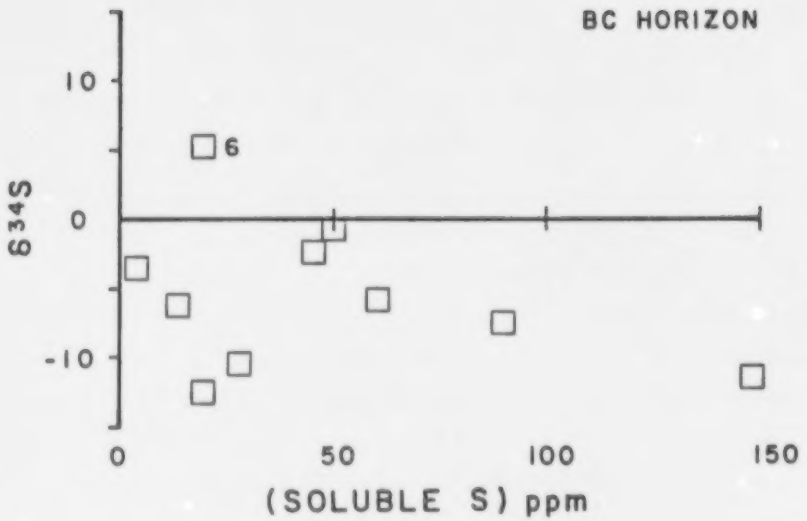

Figure 22. $\delta^{34}S$ vs. concentration of soluble sulphur in the BC horizon. Site 6 is tilled so that it may contain sulphur derived from higher horizons. All other $\delta^{34}S$ values are negative.

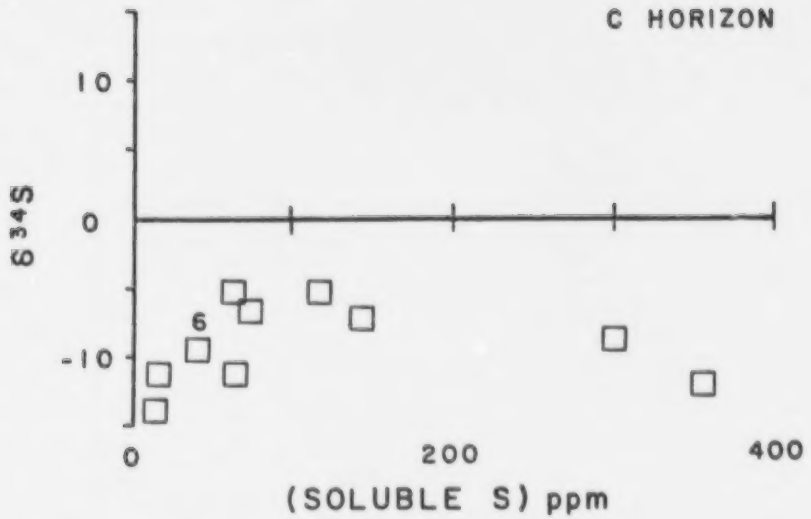

Figure 23. $\delta^{34}S$ vs. concentration of soluble sulphur in the C horizon.

When $\delta^{34}S$ values are compared to concentration for the total sulphur in the LFH horizon, no clear relationship could be found. Sites 1, 2, 3, and 15, which are close to the source of emissions, have the highest $\delta^{34}S$ values (Figure 24). The $\delta^{34}S$ value for total sulphur is lower than that of soluble sulphur at the same sites (Figure 25). This is consistent with the minor soluble sulphur component deriving much of its sulphur from the atmosphere. The major insoluble form, which consists mainly of vegetation debris, probably derived a significant proportion of its sulphur from the sub-soil and, hence, has lower $\delta^{34}S$ values.

The patterns of soil $\delta^{34}S$ values with depth and location are depicted in Figures 26 and 27. Figure 26 shows that the $\delta^{34}S$ values were generally lower in deeper soil horizons and with increasing distance from the stack.

From Figure 26, it would appear that the range of -10 to -12 $^{o}/_{oo}$ is representative of the pre-industrial $\delta^{34}S$ value for sulphur in the deeper horizons. Two other pieces of evidence which suggest that this range is a good choice for the pre-industrial $\delta^{34}S$ value are the isotopic compositions of total sulphur in deeper horizons and the minimum $\delta^{34}S$ values of surface waters (Figure 14).

If it is assumed that the pre-industrial $\delta^{34}S$ value for sulphur in the deeper horizons was -10 $^{o}/_{oo}$, it seems that industrial sulphur has penetrated as deeply as the C horizon and elevated the associated $\delta^{34}S$ value by at least 5 $^{o}/_{oo}$. A simple isotope-mass balance calculation indicates that, within 5 km of the stack, about one-third of the soluble S in the deep horizons is derived from industrial emissions. Beyond 8 km from the stack, the industrial contributions to the deepest soil horizons are almost negligible.

The shallower layers have even higher contributions from the industrial sulphur input. With the assumption that, during the pre-industrial phase upper horizons had the same $\delta^{34}S$ values as the lower horizons, the soluble sulphur in the LFH layer within 2 km of the plant would primarily be of industrial origin, while at 10 km the industrial component decreases to roughly 50 percent. With the same assumption,

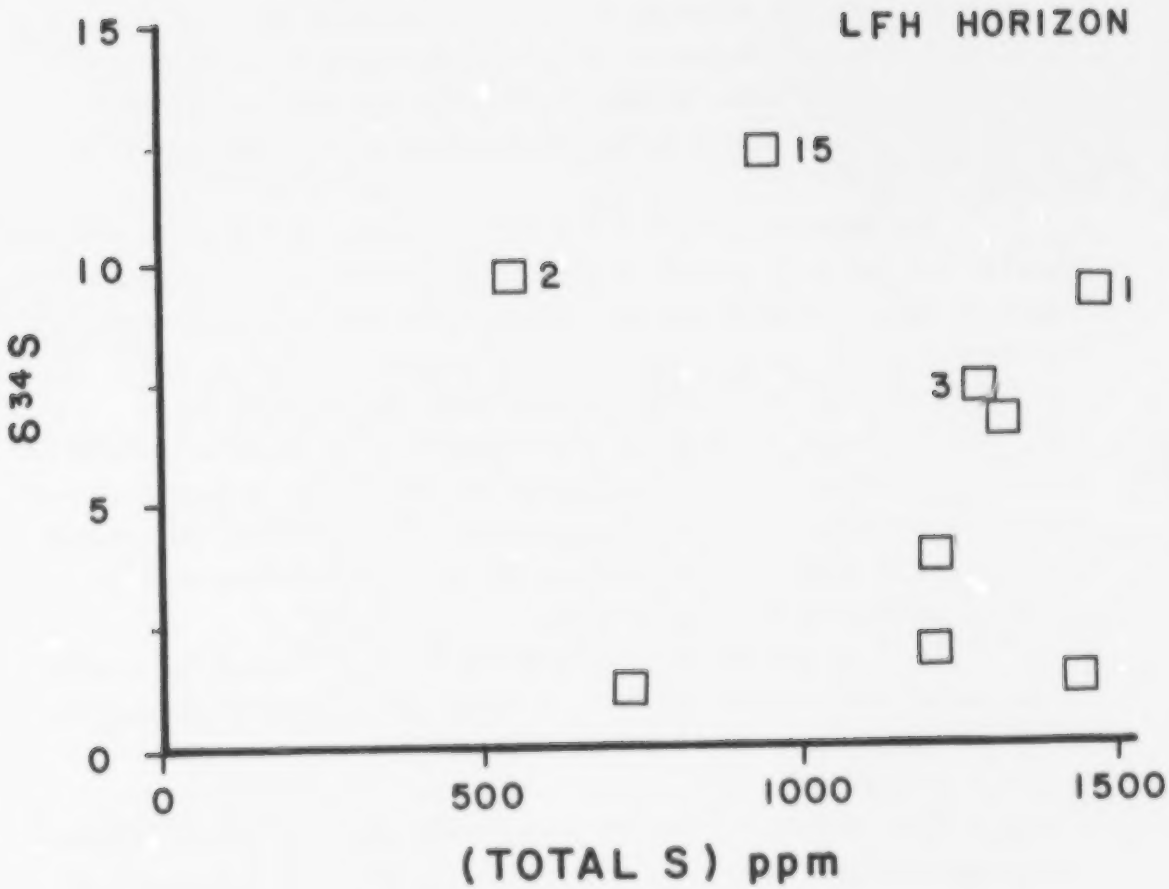

Figure 24. $\delta^{34}S$ vs. concentration of total sulphur in the LFH horizon. Sites 1, 2, 3, and 15 are closer to the flare stack and tend to have higher $\delta^{34}S$ values although they do not exceed the stack value (+17 °/oo).

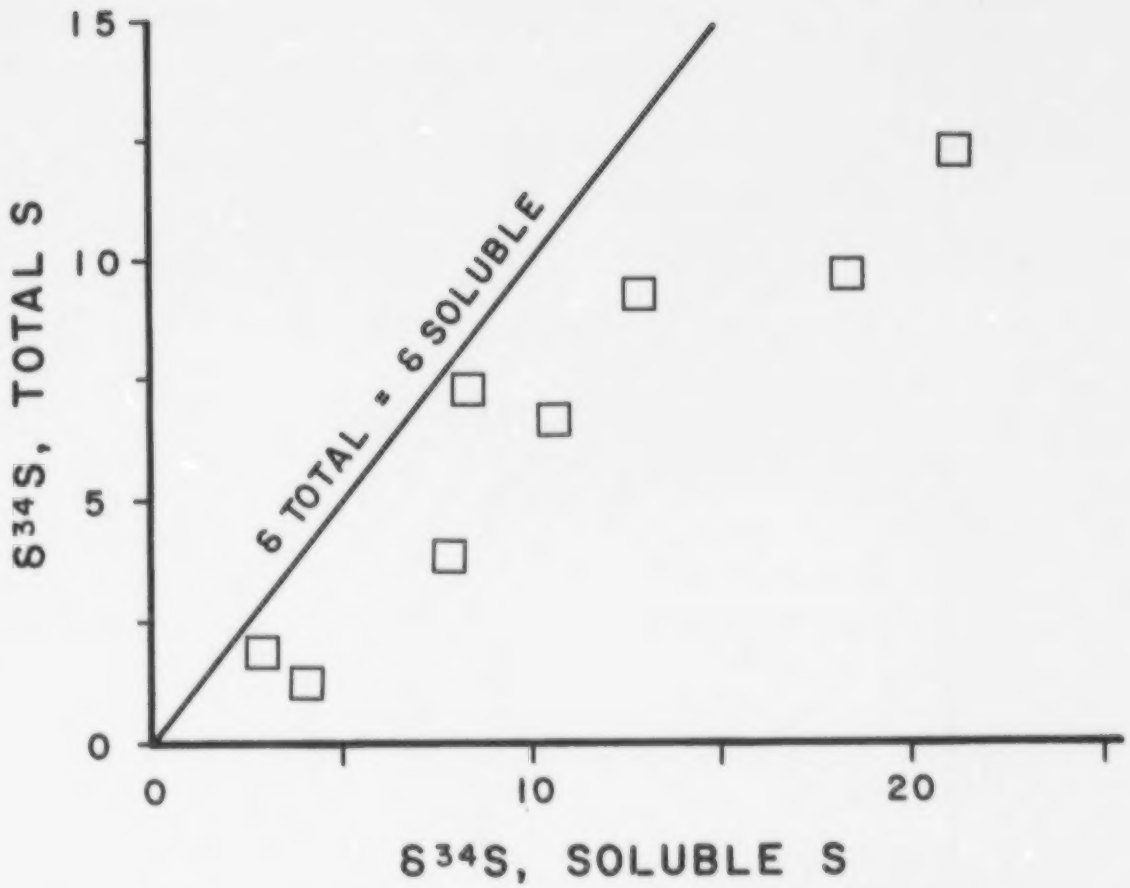

Figure 25. $\delta^{34}S$ for total sulphur vs. the $\delta^{34}S$ for soluble sulphur in the LFH horizon. The $\delta^{34}S$ value of the total sulphur is lower than the $\delta^{34}S$ values for soluble sulphur at a given site. This suggests that most of the soluble sulphur in the upper layer comes from the atmosphere while the insoluble component consists mainly of vegetation debris which probably derived some of its sulphur from deeper soil layers.

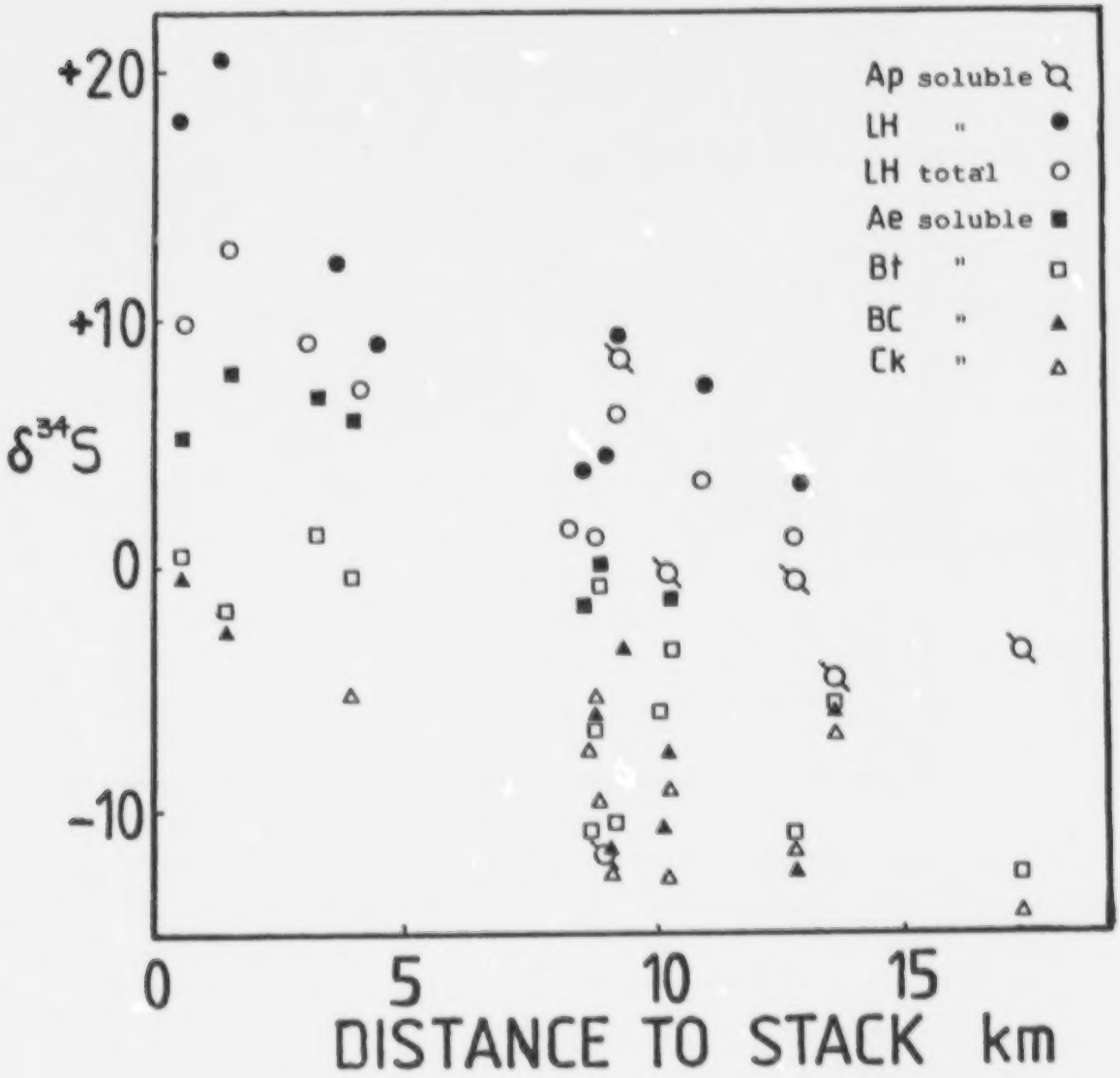

Figure 26. $\delta^{34}S$ values for different soil horizons as a function of distance from the stack. The $\delta^{34}S$ values generally decrease with depth and also decrease with increasing distance from the stack.

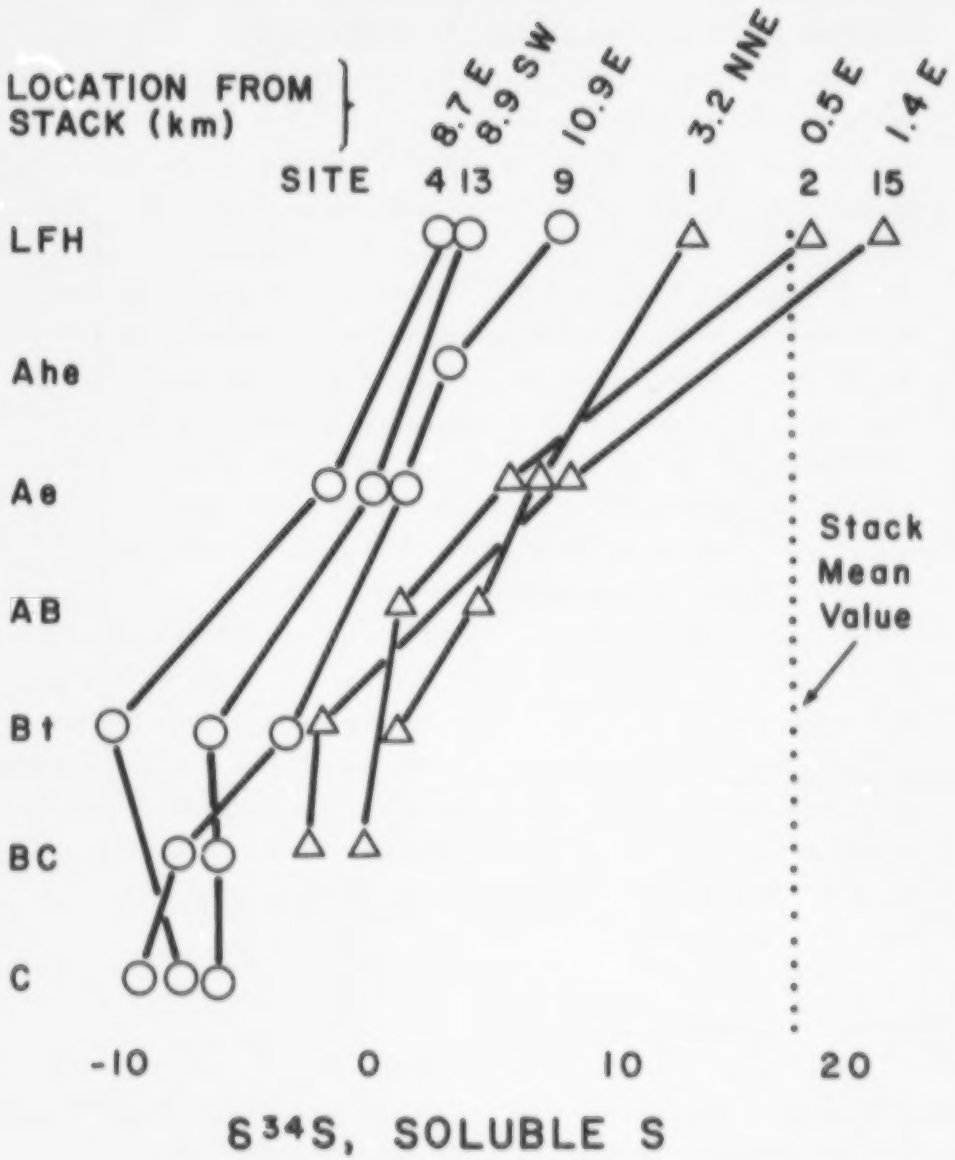

Figure 27. $\delta^{34}S$ values of different soil horizons for three sites near (Δ) and three sites farther away (0) from the flare stack. At all sites, $\delta^{34}S$ decreases with depth, the rate of change being greatest for those sites near the stack, because the average $\delta^{34}S$ value of their LFH layers is 12‰ higher than that of the sites farther away.

the industrial contribution to total sulphur in the uppermost LFH horizons is somewhat less than for soluble sulphur, reaching a maximum of about 80 percent within 2 km of the plant. It would appear that a suitable undisturbed reference or control site was not located far enough away from the stack for the $\delta^{34}S$ values of the upper horizons to asymptotically approach the pre-industrial value. The $\delta^{34}S$ was +2.9 °/oo in the LFH horizon at site 11, 13 km east of the stack. The $\delta^{34}S$ values as low as -120 °/oo (site 12) were found for Ap horizons but this may be the consequence of ploughing into the deeper Bt and/or BC horizons. Even if one carries out similar isotope-mass balance calculations for the LFH horizons based on +2.9 °/oo being the pre-industrial value, the industrial component in this layer is still substantial, comprising 50 percent of the total about 5 km from the plant (as compared to 10 km with -12 °/oo as the reference).

Figure 27 has been presented to examine the difference between three sites close (1, 2, 15) and three sites farther away (4, 9, 13) from the flare stack. The $\delta^{34}S$ values for the LFH layer of the sites closer to the stack are about 7 °/oo higher on the average than for the sites farther away. At all sites, $\delta^{34}S$ decreased with depth, the rate of change being greater for those sites near the stack because of the presence of larger proportions of industrial sulphur in the shallow layers.

4.6 VEGETATION

4.6.1 Epiphytic Lichens

Tissue sulphur concentrations and $\delta^{34}S$ values for lichens growing on trembling aspen are given in Appendix 9.10 and Figures 28 and 29. It should be pointed out that the sample size (n) was not sufficient to facilitate definitive conclusions, with due consideration of the inherent biological variation.

No definite relationship could be established between the distance from the flare stack at which the individual sampling plots are located and the variability in soluble sulphur content for *Parmelia sulcata* or *Hypogymnia physodes* (Figures 28 and 29). There is, however,

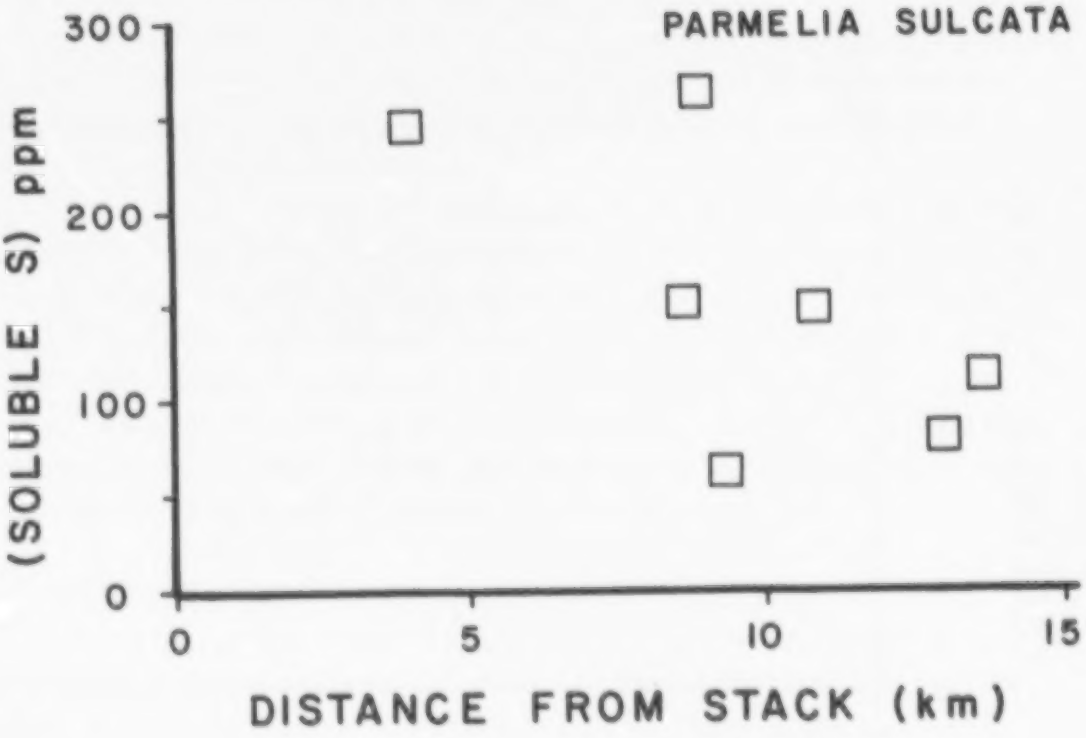

Figure 28. Concentration of soluble sulphur in *Parmelia sulcata* vs. distance from the stack.

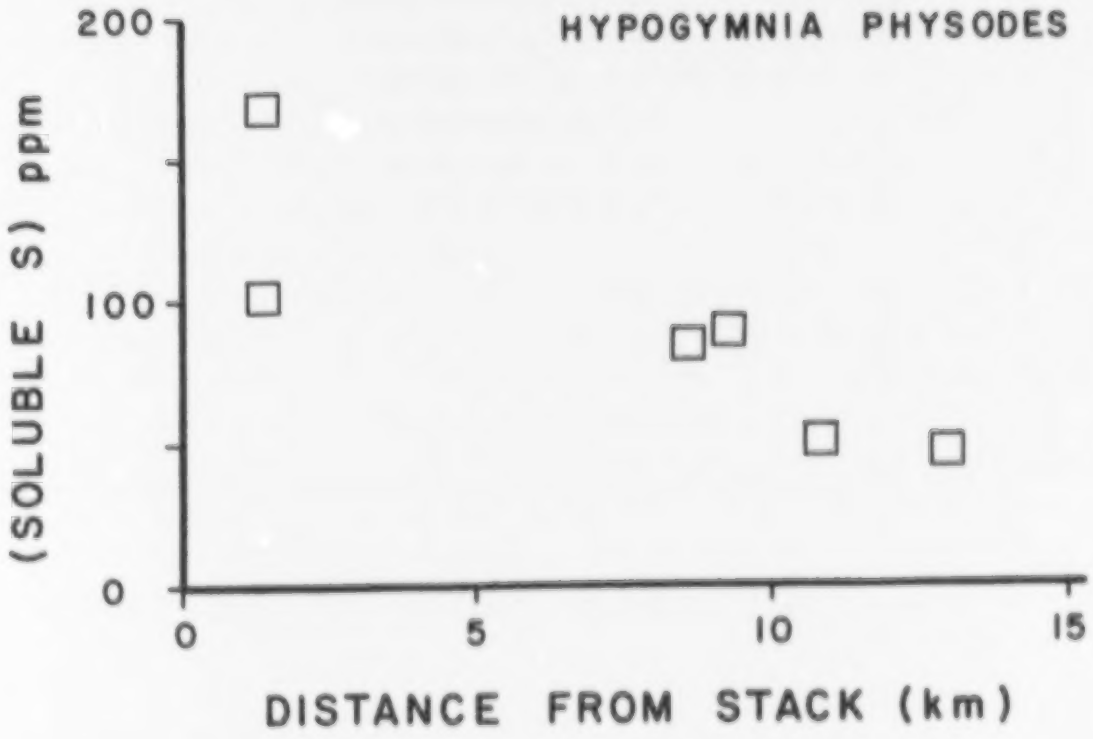

Figure 29. Concentration of soluble sulphur *Hypogymnia physodes* vs. distance from the stack.

a tendency for less scatter in the values of tissue S content of *H. physodes*. This most likely relates to the fact that the latter does not have rhizines to trap debris and pieces of substrate.

The total tissue sulphur of these lichens also did not correlate well with distance from the flare stack. For sites 1 and 2, which are very close to the stack, the total sulphur content was not as high as the sites further away. This, however, may be due to a breakdown of the integrity of the cells structure and consequent loss of their contents. Similar types of response have been reported by other workers (Richardson and Nieboer 1981).

All $\delta^{34}S$ values for soluble and total sulphur in tree dwelling lichens were positive, indicating little or no uptake of sulphur originating from windblown soil particles. In 75 percent of the cases, the $\delta^{34}S$ values of the soluble sulphur were more positive than those of the total sulphur (Figure 30). This has been noted by the authors in other areas of Alberta, and may be the result of isotopic fractionation during sulphur fixation. Total and soluble sulphur $\delta^{34}S$ values are not apparently correlated with concentration measurements.

4.6.2 Aspen (*Populus tremuloides*)

The sulphur concentrations and $\delta^{34}S$ values for aspen leaves collected in the study area are given in Appendix 9.10 (Table 18). The data reveal that the leaves contain mostly insoluble sulphur, with the soluble sulphur accounting for only a small fraction of the total.

Neither soluble nor total sulphur concentration appeared to be correlated with distance from the flare stack. It is interesting to note that at site 2, which was closest to the flare stack site, both the soluble and total sulphur concentrations were lower than the average for all other sites. Again, caution should be used in examining this data, since the sample size (n) in the study is very small.

The $\delta^{34}S$ values for soluble and total sulphur appear to decrease with distance from the stack (Figures 31 and 32). Unfortunately, interpretation is confounded by the fact that the samples from the most

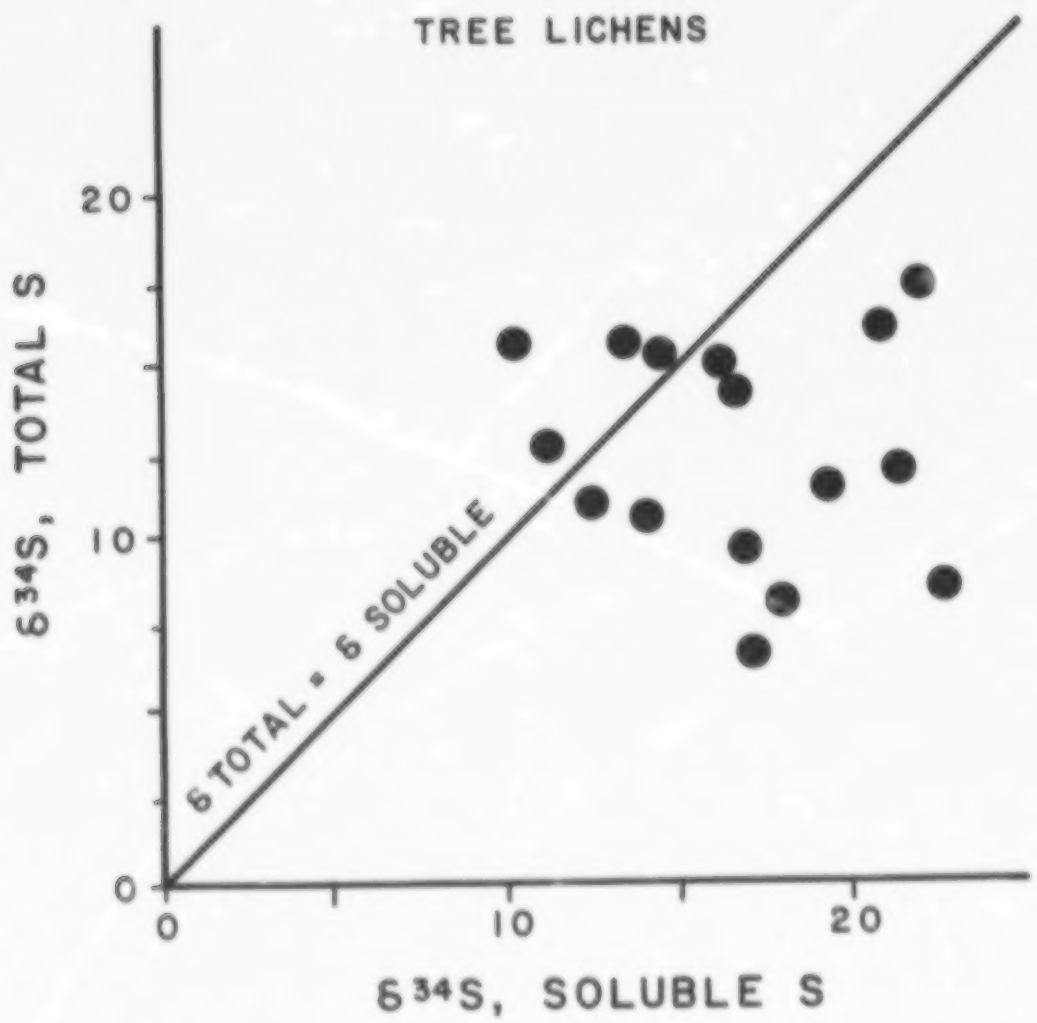

Figure 30. $\delta^{34}S$ for total sulphur vs. $\delta^{34}S$ for soluble sulphur in tree lichens.

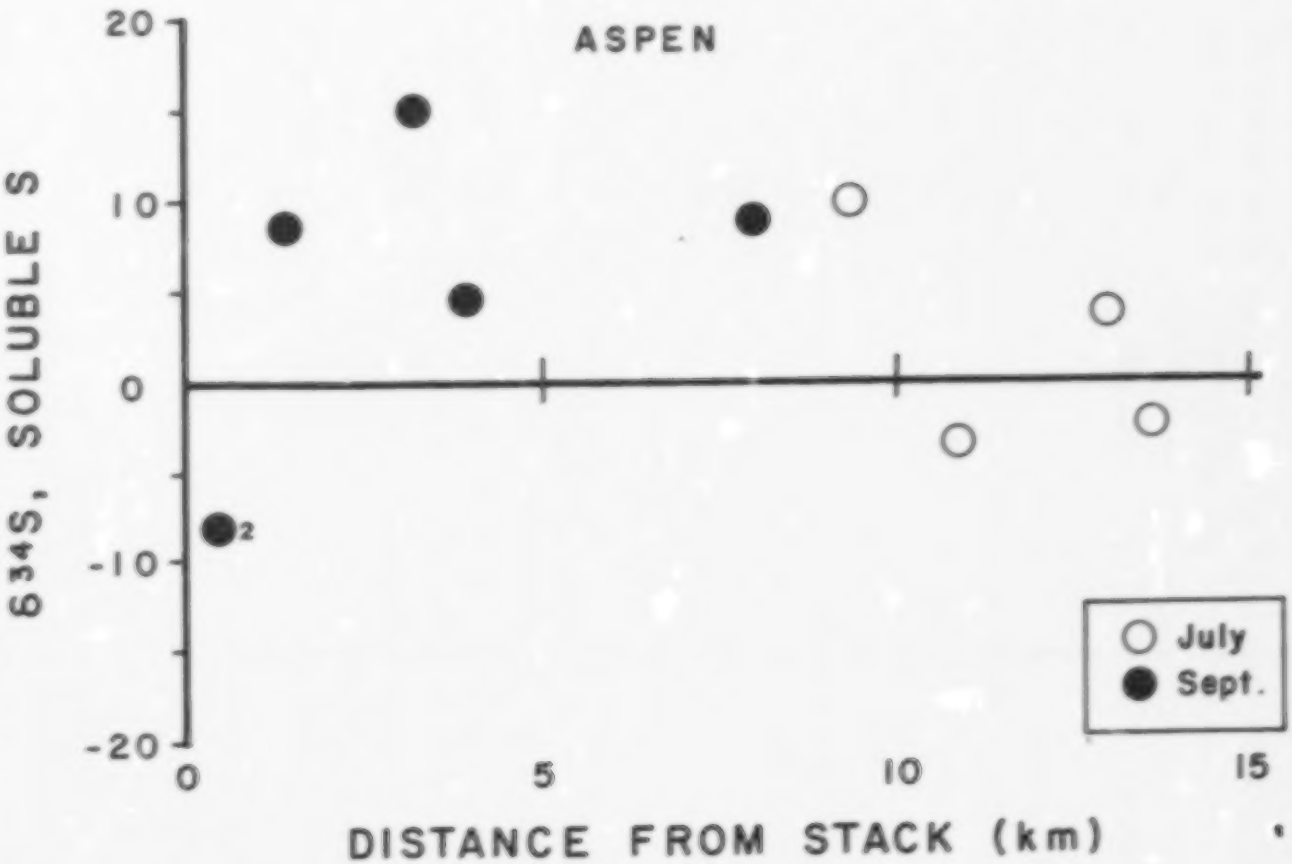

Figure 31. $\delta^{34}S$ value of soluble sulphur in aspen leaves vs. distance from stack. With the exception of site 2 which has been found anomalous in many ways, there appears to be a general decrease in $\delta^{34}S$ with distance. It is noted, however, that the differences in the time of sample collection are a critical factor.

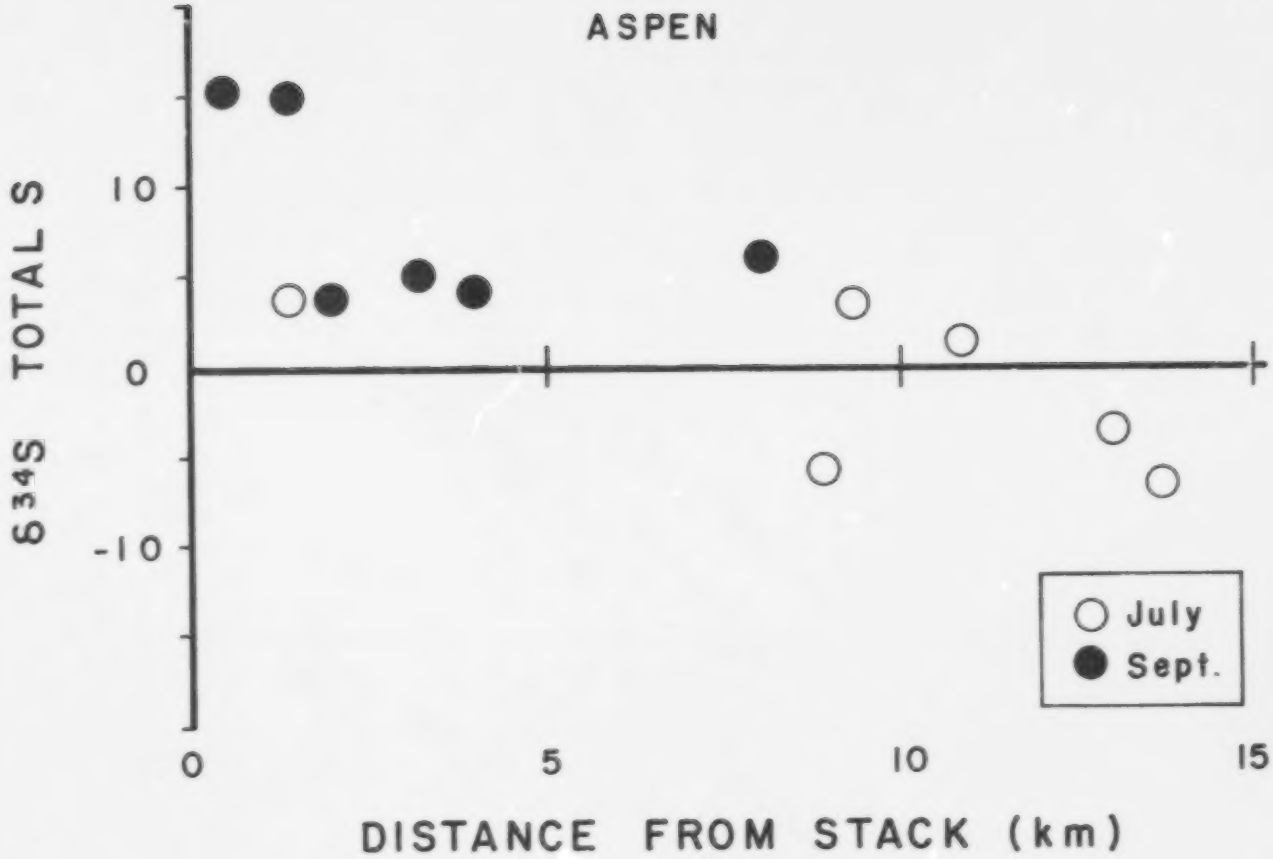

Figure 32. $\delta^{34}S$ value of total sulphur in aspen leaves vs. distance from stack. (See comments, Figure 31).

distant sites were collected in July, whereas the sites nearest the stack were sampled in September. Although the distance trend is hinted if the data for each time are viewed separately, the seasonal influence is considerable. The aspen sampled at site 15 in September had a $\delta^{34}S$ value (Figure 32). This isotopic shift is consistent with the concentration shift (Appendix 9.10, Table 18).

The $\delta^{34}S$ values of the soluble fraction in composite samples of aspen leaves show a general increase in the concentration of the soluble S (Figure 33).

4.6.3 Ground Lichens and Mosses

Sulphur SIRA and concentration data are given in Appendix 9.10 (Table 19). Composite samples of each plant species were collected at a site close to the stack and at a remote site.

The $\delta^{34}S$ values of all specimens were positive, ranging from +7 to +17°/oo , indicative of considerable uptake of atmospheric sulphur compounds.

For *Pleurozium schreberi* (a moss) and *Cladonia* sp. (a lichen) the $\delta^{34}S$ value for total sulphur was nearly 5°/oo lower at the distant site than at the site closer to the stack. On the other hand, *Peltigera aphthosa* had similar $\delta^{34}S$ values (+11 and +10°/oo) at the near and distant sites. This may reflect the different biochemical properties of the latter, which is associated with a blue-green N-fixing alga, or it may be due to the subtle differences in the habitat.

4.7 FERTILIZERS

The $\delta^{34}S$ data for the trace sulphur component in the fertilizers collected in the study are presented in Appendix 9.10 (Table 20). They ranged from +10 to +18°/oo, which suggests that the fertilizers were manufactured in Alberta. The influence of these small quantities of sulphur in fertilizers would have little effect on the additions of industrial sulphur to the soils, even with many years of their application (A.W. Jaeggi, pers. comm.).

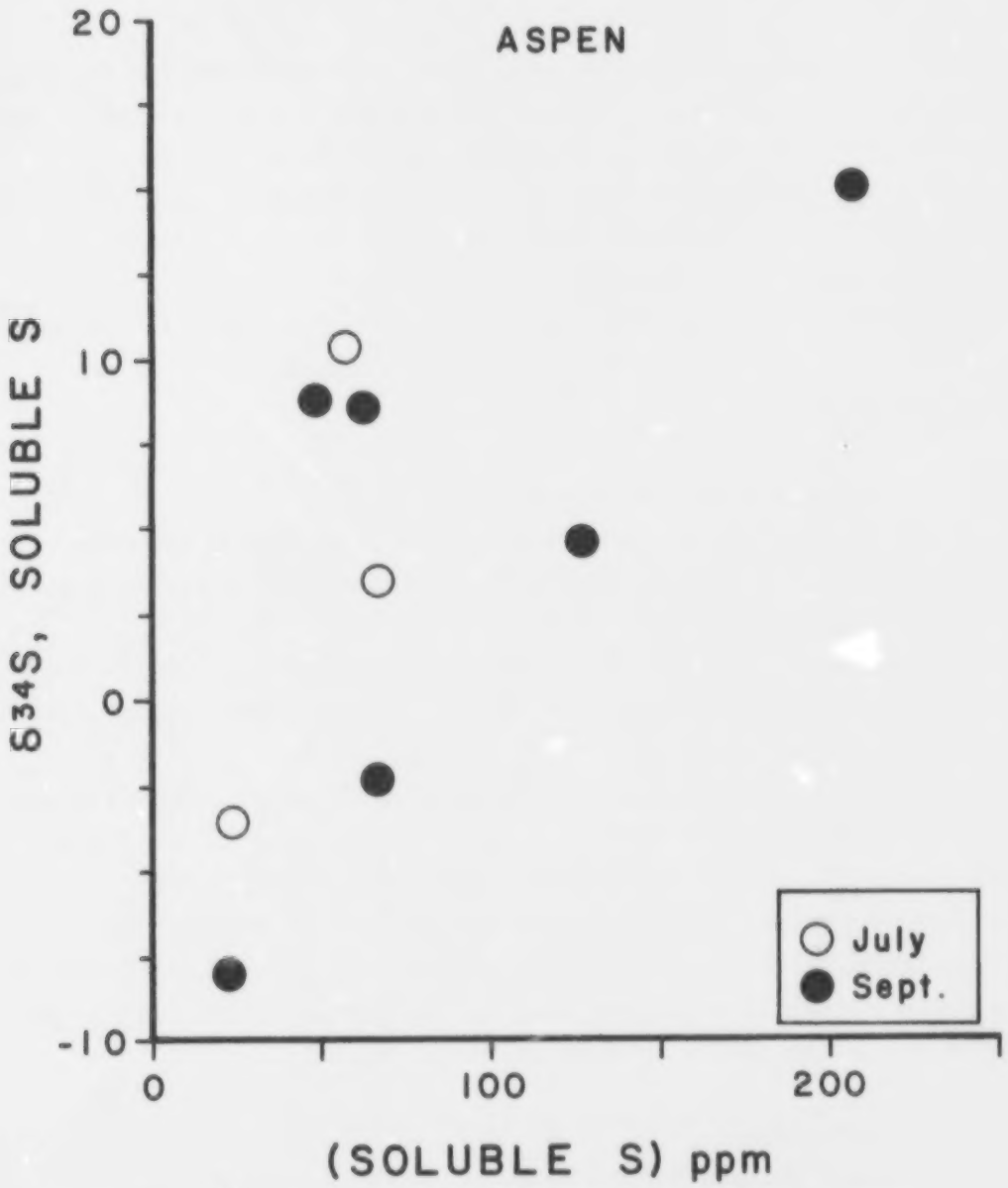

Figure 33. $\delta^{34}S$ vs. concentration of soluble sulphur in aspen leaves.

4.8 PRODUCED CROP SEED

Rapeseed, wheat, and oats from the Valleyview area were analysed by sulphur SIRA analysis (Appendix 9.10, Table 21). The $\delta^{34}S$ values for total sulphur in six rapeseed samples ranged from -2.8 to -16.5^{o}/oo. Their total sulphur content varied from 1882 to 3881 ppm. Two samples of wheat and two samples of oats had $\delta^{34}S$ values of (-3.1 and -8.6) and (-5.9 and -12.5)^{o}/oo, respectively. Within the constraints of the value of the limited number of samples analysed and their variability, the industrial sulphur component in the seeds appeared to be minor. The $\delta^{34}S$ values of the seeds were in the same general range as soluble sulphur in Ap and lower soil horizons.

5. CONCLUSIONS

1. Emissions from the flaring operation (now inactive) at the Amerada-Hess processing plant near Valleyview, Alberta were found to have a sample mean $\delta^{34}S$ value of +17 °/oo. In contrast, the pre-industrial $\delta^{34}S$ value for the surrounding environment was estimated to be -10 °/oo. Thus, the situation was favourable for using sulphur isotope abundances to examine the proportion of sulphur of industrial origin in the environment.
2. Although the overall concentration of atmospheric sulphur-containing particulates was not noticeably reduced when flaring ceased, the measured concentration of wind-borne particulate S, specifically from the direction of the Amerada plant site, decreased significantly.
3. The concentration of atmospheric SO_2 decreased when flaring ceased.
4. When the flaring was active, the $\delta^{34}S$ values of S-containing particulates and SO_2 were similar to that of the stack gas.
5. The $\delta^{34}S$ values for both S-containing particulates and SO_2 decreased markedly after flaring ceased, except in the SSE direction at the Dallman and Gourlay farms.
6. Isotope data suggest at least three sources of sulphur compounds in the composite wet and dryfall samples. While flaring was active, higher concentrations of sulphur compounds present in the bulk deposition samples had $\delta^{34}S$ values near that of the emissions. A second source appeared to be wind-blown dust. An unidentified third source was associated with $\delta^{34}S$ values near +22 °/oo.
7. High concentrations of soluble S-compounds in dugouts and ponds were associated with $\delta^{34}S$ values close to that of the flare stack emissions. In dugouts and ponds with low S-concentrations, the associated $\delta^{34}S$ values were very similar to those measured for deep soil horizons.

8. With the exception of site 2 (very close to the flare stack), the pH of the Ae soil horizon decreased with increase in soluble sulphur concentration.
9. The pH of the C horizon was slightly alkaline at all sites, while the overlying horizons were, in general, slightly acidic.
10. With the exception of sites 1 and 15, the concentration of soluble sulphur in the Ae soil horizon was low and decreased with distance from the stack. Soils at sites 1 and 15 were derived from sand deposited over till, while the other sites had much higher clay content.
11. The soluble sulphur content of the samples from the C horizon was generally higher (sometimes by almost an order of magnitude) than that of overlying horizons.
12. The $\delta^{34}S$ values and concentrations of soluble sulphur in upper soil horizons generally increased in response to inputs of industrial sulphur.
13. The $\delta^{34}S$ values for soluble sulphur concentrations in lower soil horizons generally decreased as S concentration increased. This is indicative of sub-surface sources with $\delta^{34}S$ values in the range -10 to -12 $^{o}/_{oo}$.
14. The $\delta^{34}S$ values of soluble sulphur in all soil horizons were found to decrease with distance from the flare stack. This tendency was less pronounced with soil depth. These observations are consistent with the penetration of industrial sulphur compounds with positive $\delta^{34}S$ values into an environment with indigenous negative $\delta^{34}S$ values.
15. The soluble sulphur content of tree dwelling lichens (*Hypogymnia*) generally appeared to decrease with distance from the flare stack.
16. The $\delta^{34}S$ values for tree dwelling lichens were all positive, falling within the range of atmospheric SO_2 and particulates. There was no clear relationship between $\delta^{34}S$ value and S concentration.

17. $\delta^{34}S$ values of a limited number of ground lichens and mosses were in the range +7 to +17 $^{o}/_{oo}$. This is most likely due to the uptake of atmospheric sulphur compounds of industrial origin.
18. Neither the soluble or total sulphur concentration in aspen leaves showed a consistent relationship with the distance of the plot location from the flare stack.
19. The $\delta^{34}S$ values for total sulphur in aspen leaves sampled during September were generally more positive than samples collected in July, and the overall pooled data showed a general tendency to decrease with distance.
20. The sulphur isotope data reveal that sulphur of industrial origin is a very minor component in crop seeds.

6. COMPARISON OF THE VALLEYVIEW AND TEEPEE CREEK STUDIES

It is useful to compare data from the Teepee Creek area (representing a location where a relatively small source of emissions had just commenced) with the Valleyview area (where a flaring operation has ceased after 26 years of operation). Unfortunately, in making the comparison, there are some data gaps. However, Table 1 summarizes a comparison of data from the two studies.

In making the comparison, it must be noted that the isotopic references are significantly different. The stack emissions of Teepee Creek had $\delta^{34}S$ values of +24 °/oo, as compared to +17 °/oo for the flaring operation at Valleyview. Somewhat more negative $\delta^{34}S$ values were encountered in the deeper soil horizons at Teepee Creek than at Valleyview.

The fact that the emissions (as indicated by the $\delta^{34}S$ values) at Teepee Creek represent a minor input to the atmosphere as compared to those at Valleyview, is immediately evident in Table 1. The average $\delta^{34}S$ value of the atmosphere for the Teepee Creek area was +8 °/oo (with the emissions at +24 °/oo). In the Valleyview area, the average $\delta^{34}S$ value of the atmosphere was +16 °/oo (with the emissions near +17 °/oo).

The total sulphur in the uppermost soil horizons had average $\delta^{34}S$ values of -13 and +6 °/oo at Teepee Creek and Valleyview, respectively. While mass balance calculations of the industrial contributions depend upon the pre-industrial $\delta^{34}S$ value chosen, it was apparent that industrial sulphur comprised on the average about 50 percent of the total sulphur in the uppermost horizon at the sites sampled in the Valleyview area. In contrast, the presence of industrial sulphur in comparable horizons at Teepee Creek could not be demonstrated. The soluble sulphur component in the same horizons at Teepee Creek had an average $\delta^{34}S$ value of +1 °/oo, as compared to +11 °/oo at Valleyview. This suggests a much higher total accumulation of industrial sulphur at Valleyview. It should be noted that the soluble S component in the soil is a small fraction of the total sulphur and also the most mobile. Therefore, the value of +1 °/oo at Teepee Creek might signify the

beginning of the contributions of industrial sulphur to the soil. The $\delta^{34}S$ value of upper soil horizons appeared to increase with sulphur concentration at Valleyview. However, at Teepee Creek the $\delta^{34}S$ values decreased with increase in S concentration. The Valleyview situation was indicative of the accumulation of industrial S input, while the data from Teepee Creek were characteristic of a soil component dominated by negative $\delta^{34}S$ values. In both study areas, the $\delta^{34}S$ values of the soluble S in the deeper soil horizons generally became more negative with increasing S concentration, suggesting similar sub-surface sulphur sources.

The concentration data are consistent with conclusions based on sulphur isotope abundances. Both the soluble and total sulphur contents are higher in the upper soil horizons at Valleyview than at Teepee Creek (Krouse and Case 1981). However, soluble sulphur concentrations in the C horizons at both areas are comparable.

On the average, the soluble and total sulphur in aspen leaves at Valleyview were 8 and 10 $^{o}/_{oo}$ more enriched in ^{34}S in comparison to Teepee Creek.

In summary, concentration and isotopic data reveal that the pre-industrial environments of both areas were similar. One apparent discrepancy was that the average $\delta^{34}S$ value of the deeper soil horizons at Teepee Creek was more negative compared to Valleyview. We attribute this difference in isotopic composition to the natural variability of the parent soil material and the pedogenic processes, rather than to substantial contributions of sulphur of industrial origin to the C horizon. In contrast to the Teepee Creek area, concentration and sulphur isotope data for Valleyview provide evidence for the presence of substantial amounts of industrial sulphur in the atmosphere, hydrosphere, vegetation, and upper soil horizons.

Table 1. Comparison of mean $\delta^{34}S$ values for environmental constituents in the Teepee Creek and Valleyview areas of Alberta.

Component	$\delta^{34}S$ Teepee Creek	$\delta^{34}S$ Valleyview
Stack Emissions	+24	+17
Atmospheric SO_2	+ 8	+16
Aspen (Soluble)	- 4	+ 4
Aspen (Total)	- 7	+ 3
Soil (Horizons)		
LFH-Ah (Soluble)	+ 1	+11
(Total)	-13	+ 6
Ae (Soluble)	- 7	+ 3
Bt (Soluble)	-14	- 5
C (Soluble)	-19	-10

7. RECOMMENDATIONS

There has been a tendency to acquire massive amounts of data on pollutant concentrations for a few specific compounds in air quality monitoring programmes. Considerable effort has been expended in modelling the dispersion of pollutants. Within the past few years, the presence of industrial sulphur compounds in the environment has been effectively documented using stable isotope relative abundances (SIRA).

While all of the above are used more or less routinely, the assessment of the actual effects of industrial emissions upon the environment is still very controversial. Since techniques for this assessment are available, the major problem is that of co-ordinating the methodologies of a number of disciplines to establish scientifically sound cause and effect relationships.

The scientific literature abounds with data from laboratory experiments on the effects of short-term exposures of high concentrations of pollutants on isolated ecosystem constituents. Extrapolation of these data to field situations where the environment has been repeatedly exposed to variable levels of pollutants over many years is tenuous at best. Therefore, one concludes that meaningful data must be obtained in field situations.

Since sour gas processing operations have been active for various times in different locations in Alberta, the province has a unique opportunity to develop a reliable and realistic environmental protection policy based on sound scientific criteria. These criteria must be established using co-ordinated multidisciplinary studies of ecosystems that have been subjected to varying degrees of pollutant exposures. The project of the West Whitecourt Environmental Study Group (co-ordinated by A. Legge and currently being published as a series of papers in Water, Air, and Soil Pollution) is well recognized as an example of the scientific returns which can be realized from a co-operative inter-disciplinary effort.

In the current study, the presence of sulphur of industrial origin in many constituents of the environment was documented using SIRA.

However, relating this presence of industrial sulphur to effects on the environment, even on the basis of simple chemical criteria, is beyond the objectives and scope of this report.

While specific recommendations pertaining to the Peace River area of Alberta emerge from the current study, it was felt that these should not be cited in isolation from the overall desirable goals cited above. Four major statements are presented along with auxiliary recommendations:

1. Co-ordinated multidisciplinary studies of the effects of sour gas processing plants on the environment should receive high priority. Specific auxiliary recommendations are:
   - 1.1 A multidisciplinary approach should be used to gather data to characterize the environment existing prior to establishing or expanding sour gas processing plants. Equivalent data should be obtained at regular intervals (3 to 5 years) throughout the lifetime of the operation and for an appropriate length of time afterwards as dictated by the data.
   - 1.2 The Teepee Creek area (representing a site where a gas processing plant recently commenced operation) should be re-examined within the next three years and the Valleyview area (representing an area where a long-term gas processing operation recently ceased) should also be evaluated within the next five years.
   - 1.3 Certain data gaps (e.g., soil properties) should be filled to provide a more meaningful comparison between the Teepee Creek and Valleyview areas.
   - 1.4 As new relevant methodology is developed, its applications should be given serious consideration in the above recommendations.
2. The effects of sour gas processing plant emissions on agricultural and native soils should be examined in the light of changes in soil chemistry and microbiology.

2.1 The procedure of adding sulphuric acid and noting pH changes provides, at best, only a crude approximation of a soil's buffering capacity. In the soils section of the present report, it is stated that 1 meq H^+/100 gm of soil depressed the pH of upper horizons by roughly 2 units. It is unrealistic to relate this change (due to relatively large H^+ concentration over a short time) to the long-term consequences of the additions of lower concentrations of H^+, particularly where processes such as leaching and bacterial conversions undoubtedly occur. Better laboratory procedures for assessing soil response to acid emissions are needed. Such studies are presently in progress (private communication, Dr. D.N. Graveland, Alberta Environment, Earth Sciences Division, Lethbridge).

2.2 Specific chemical and biochemical buffering systems should be better documented for all soil horizons.

2.3 The effects of industrial emissions on the chemical and biological properties of agricultural soil should not be evaluated without considering agricultural practices, especially tillage and fertilization.

2.4 The isotopic compositions of different soil sulphur constituents should be further investigated.

3. The behaviour of sulphur compounds in vegetation should receive intensive study in order to better understand the effects of sour gas plant emissions on productivity.

3.1 As in soils (Recommendation 2.2), the more mobile soluble sulphur component of plant tissue tends to be slightly more enriched in ^{34}S than insoluble organic sulphur compounds. The significance of this phenomenon should be further explored.

3.2 The variation of foliar sulphur $\delta^{34}S$ values with season should be documented.

3.3 A better understanding of the mechanisms of atmospheric sulphur uptake and translocation within plants should be obtained.

4. Atmospheric monitoring of sulphur compounds should be pursued more efficiently.

4.1 Sites for atmospheric sampling (using standardized protocol) should be selected on the basis of a preliminary inventory of pollution-sensitive plant species.

4.2 The efficiency and flexibility of the wind directionally controlled pollutant sampling array should be increased.

4.3 Sampling devices should be used to collect precipitation separately as wetfall. This would eliminate collection of sulphur compounds resulting from dry deposition. Ideally, the wet precipitation collection should be integrated with the dryfall sampling.

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9. APPENDICES

9.1 AMERADA-HESS GAS PRODUCTION FIGURES, 1952 to 1979

Gas production figures for the Amerada-Hess Sturgeon Lake Plant 1952 to 1979 (as communicated by Bill Wylie, Energy Resources Conservation Board of Alberta are given in Tables 2 and 3. Production occurred at each of two batteries (16-31071-23 W5M and 10-2971-23 W5M) up to 1977. Since June 1978, all production has been at one central battery (10-29-71-23 W5M). Essentially all gas produced was flared until May 1980. At each battery, some gas was used as lease fuel but it still resulted in being burned in treaters and line heaters with SO_2 released through the stacks. In May 1980, a line to the Sturgeon Lake South Gas Plant was completed to conserve and process the gas.

Table 2. Gas production at Battery 16-31-71-23 W5M, Amerada-Hess Sturgeon Lake Plant.

Wells:

9-31-71-23	W5M	3-6-72-23	W5M
13-32-71-23	W5M	5-6-72-23	W5M
1-6-72-23	W5M	7-6-72-73	W5M

Year	Gas Production x 10^3 m^3	Sulphur Emission t/d
1954	8.5	.003
1955	220.2	.03
1956	3 055.2	1.013
1957	3 900.4	1.293
1958	4 029.9	1.336
1959	5 145.4	1.706
1960	4 345.8	1.441
1961	5 246.7	1.740
1962	5 669.2	1.880
1963	11 015.1	3.652
1964	4 255.8	1.743
1965	4 867.9	1.614
1966	5 218.0	1.730
1967	4 919.2	1.631
1968	4 098.2	1.359
1969	4 316.5	1.431
1970	3 872.7	1.284
1971	5 547.6	1.839
1972	8 383.3	2.779
1973	17 115.6	5.675
1974	15 389.8	5.102
1975	9 796.1	3.248
1976	8 107.0	2.688
1977	8 419.8	2.792
	Total	17 925.51 t/24 yr

Table 3. Gas production at Battery 10-29-71-23 W5M, Amerada-Hess Sturgeon Lake Plant.

Wells:

11-16-7-23 W5M	9-29-71-23 W5M
3-21-7-23 W5M	5-32-71-23 W5M
11-21-7-23 W5M	7-32-71-23 W5M
13-21-7-23 W5M	11-32-71-23 W5M
5-28-7-23 W5M	15-29-71-23 W5M

Year	Gas Production x 10^3 m^3	Sulphur Emission t/d
1952	26.7	.009
1953	286.7	.004
1954	13.8	.352
1955	1 062.1	2.073
1956	6 253.6	2.521
1957	7 602.4	2.328
1958	7 021.2	3.001
1959	9 051.6	2.641
1960	7 964.8	3.089
1961	9 315.9	2.614
1962	7 883.7	2.418
1963	7 291.8	2.330
1964	7 028.3	2.339
1965	7 054.2	2.532
1966	7 636.5	2.923
1967	8 815.6	2.821
1968	8 509.1	3.264
1969	9 846.3	4.318
1970	13 025.2	4.450
1971	13 422.9	5.930
1972	17 886.3	10.931
1973	32 968.9	8.518
1974	25 690.4	4.396
1975	13 257.6	3.732
1976	11 257.0	3.747
1977	11 302.4	
Consolidation of Batteries 16-31 and 10-29		
1978	17 240.6	5.716
1979	21 040.5	6.976
	Total	35 088.84 t/28 yr
		17 915.51
	Grand Total	53 004.35 t

9.2 LOCATIONS OF SAMPLE COLLECTION SITES IN THE VALLEYVIEW AREA, ALBERTA

Locations of sample collection sites in the Valleyview area:

1. LSD 16-5-72-23 W5M; 2 mi. (3.2 km) NNE of flare stack; few lichens present on trembling aspen; elev. 2900 ft. (884 m).
2. LSD 1-32-71-23; 0.3 mi. (0.5 km) E of flare stack; no lichens present on trembling aspen and very few on ground; symptoms of air pollution injury evident on leaves of trees and shrubs; strong "sulphur" odour in air; elev. 2600 ft. (792 m).
3. LSD 14-16-71-16 W5M; 2.5 mi. (4.0 km) SE of flare stack; epiphytic fruitcose lichens and some foliose lichens exhibited typical air pollution injury; elev. 2400 ft. (731 m).
4. LSD 1-31-71-22 W5M; 5.4 mi. (8.7 km) SE of flare stack; luxuriant lichen development on trembling aspen; no air pollution injury symptoms noted on vascular or non-vascular vegetation; elev. 2450 ft. (747 m).
5. LSD 12-32-71-22 W5M; 5.8 mi. (9.3 km) E of flare stack; cultivated field; elev. 2450 ft. (747 m).
6. LSD 8-6-72-22 W5M; 5.5 mi (8.9 km) ENE of flare stack; cultivated field; elev. 2550 ft. (777 m).
7. LSD 5-5-72-22 W5M; 5.9 mi. (9.5 km) E of flare stack; lichens on aspen well developed; no air pollution injury symptoms noted on vascular or non-vascular vegetation; elev. 2550 fet. (777 m).
8. LSD 16-32-71-22 W5M; 6.5 mi (10.5 km) E of flare stack; noncultivated pasture; elev. 2450 ft. (747 m).
9. LSD 12-33-71-22 W5M; 6.8 mi (10.9 km) E of flare stack; lichens on aspen well developed; elev. 2400 ft. (731 m).
10. LSD 4-3-72-22 W5M; 8.0 mi (12.9 km) E of flare stack; cultivated field; elev. 2300 ft. (701 m).

11. LSD 3-3-72-22 W5M; 8.1 mi (13.0 km) E of flare stack; lichens on trembling aspen well developed; elev. 2300 ft. (701 km).
12. LSD 3-6-72-21 W5M; 11.0 mi (17.7 km) E of flare stack; cultivated field; elev. 2200 ft. (670 m).
13. LSD 15-11-71-24 W5M; 5.5 mi (8.9 km) SW of flare stack; lichens well developed on trembling aspen; elev. 2200 ft. (670 m).
14. LSD 16-35-70-25 W5M; 8.5 mi (13.7 km) SW of flare stack; cultivated field; 2350 ft. (716 m).
15. LSD 4-33-71-23 W5M; 0.9 mi (1.4 km) SE of flare stack; few lichens found on trembling aspen trees and they showed symptoms of injury; elev. 2600 ft. (792 m).
16. LSD 4-30-71-22 W5M; 4.7 mi (7.6 km) E of flare stack; some lichens discoloured; elev. 2450 ft (747 m).
17. LSD 13-21-71-23 W5M; 1.2 mi (2 km) SSE of flare stack; few epiphytic lichens found, and those showed injury symptoms; elev. 2500 ft. (762 m).

9.3 RESUME OF SOILS BY PEDOLOGY CONSULTANTS

A resume of soils sampled from the Valleyview area by Pedology Consultants is presented in Table 4.

9.3.1 General Comments Regarding Soils

9.3.1.1 Parent Materials

VVS1 - thin sand veneer over till
VVS2 - glaciolacustrine clay veneer over till
VVS3 to VVS14 inclusive - glaciolacustrine clays
VVS15 - thin sand veneer over glaciolacustrine clay veneer over till

9.3.1.2 Permeability

- soils with sandy surface veneers have greatest infiltration rate (VVS1, VVS15)
- glaciolacustrine clays are very slowly permeable

Table 4. Valleyview area soil samples.

Site Number	Soil Name	Classification	Profile Characteristics (cm)			Parent Material	Comments
VVS1	Codesa	Orthic Gray Luvisol	L-H	5 to 0			- *P. tremuloides*
			Ahe	0 to 5	FSL		- upper slope position
			Ae	5 to 12	FSL	sand over till	- moderately well drained
			AB	12 to 35	SL		
			Bt	35 to 60+	CL		
VVS2	Donnelly	Orthic Gray Luvisol	L-H	3 to 0			- *P. tremuloides*
			Ae	0 to 5	FSL		- midslope position
			AB	5 to 30	CL	glaciolacustrine	- moderately well drained
			Bt	30 to 70	C	clays over till	- very thin L-H laver
			BC	70 to 110+	CL		
VVS3	Donnelly	Orthic Gray Luvisol	L-H	5 to 0			- *P. tremuloides*
			Ae	0 to 10	VFSL		- midslope
			AB	10 to 30	C	glaciolacustrine	- moderately well to imperfectly drained
			Bt	30 to 65	HC	clays	
			Ck	65 to 110+	HC		
VVS4	"gleyed" Nampa	Gleyed Gray Solonetz	L-H	5 to 0			- *P. tremuloides*
			Ae	0 to 15	FSL		- imperfectly drained
			Bntgj	15 to 35	C	glaciolacustrine	- very firm hardpan
			BCg	35 to 70	C	clays	- abundant salt crystals in C
			Csak	70 to 110	C		
VVS5	"gleyed" Nampa	Gleyed Gray Solonetz	Ap	0 to 20	L		- cultivated
			Bntgj	20 to 40	C	glaciolacustrine	- midslope
			BC	40 to 60	C	clays	- imperfectly drained
			Csak	60 to 110+	C		

continued ...

Table 4. Continued.

Site Number	Soil Name	Classification	Profile Characteristics (cm)			Parent Material	Comments
VVS6	Nampa	Gray Solodized Solonetz	Ap	0 to 15	L		- cultivated
			Ae	15 to 18	FSL	glaciolacustrine	- very firm hardpan
			Bnt	18 to 40	C	clays	- imperfectly drained
			BC	40 to 80	C		- abundant pebbles and coal flects in C
			Csk	80 to 110+	C		
VVS7	Donnelly	Orthic Gray Luvisol	L-H	5 to 0			- *P. tremuloides*
			Ae	0 to 10	FSL	glaciolacustrine	- very weak columns in B
			AB	10 to 20	CL	clays	- non-stony
			Bt	20 to 60	C		
			BC	60 to 100+	C		
VVS8	Donnelly	Gleyed Solonetzic Gray Luvisol	Ap	0 to 15	CL		- cultivated pasture
			Btgjnj	15 to 45	C	glaciolacustrine	- lower slope
			BCg	45 to 75	C	clays	- imperfectly to poorly drained
			Ckg	75 to 100+	C		
VVS9	Donnelly	Gleyed Solonetzic Gray Luvisol	L-H	5 to 0			- *P. tremuloides*
			Ahe	0 to 5	L	glaciolacustrine	- lower slope
			Ae	5 to 20	FSL	clays	- imperfectly drained
			Btgjnj	20 to 50	C		
			BCg	50 to 85	C		
			Ckg	85+	C		
VVS10	Donnelly	Gleyed Solonetzic Gray Luvisol	Ap	0 to 20	L		- cultivated
			Btgjnj	20 to 50	C	glaciolacustrine	- lower slope
			BCg	50 to 80	C	clays	- imperfectly to poorly drained
			Ckg	80 to 110+	C		

continued ...

Table 4. Concluded.

Site Number	Soil Name	Classification	Profile Characteristics (cm)			Parent Material	Comments
VVS11			L-H	5 to 0			- *P. tremuloides*
			Ae	0 to 15	FSL	glaciolacustrine clays	- L-H and Ae sampled only
VVS12	Donnelly	Solonetzic Gray Luvisol	Ap	0 to 20	L		- cultivated
			Btnj	20 to 55	C	glaciolacustrine clays	- moderately well drained
			Csk	35 to 100+	C		
VVS13	Donnelly	Orthic Gray Luvisol	L-H	5 to 0			- *P. tremuloides*
			Ae	0 to 10	FSL		- upper slope
			AB	10 to 15	CL	glaciolacustrine clays	- moderately well drained
			Bt	15 to 60	C		
			BC	60 to 75	C		
			Ck	75 to 110+	C		
VVS14	Snipe	Luvic Gleysol intergrade to Gleyed Gray Luvisol	Ap	0 to 25	L		- cultivated
			Aeg	25 to 28	FSL	glaciolacustrine clays	- midslope
			Btg	28 to 50	C		- poorly to imperfectly drained
			BCg	50 to 75	C		
			Ckg	75 to 100	C		
VVS15	Codesa	Orthic Gray Luvisol	L-H	3 to 0			- *P. tremuloides*
			Ahe	0 to 2	L	sand over	- upper slope
			Ae	2 to 20	FSL	glaciolacustrine	- moderately well drained
			Bt	20 to 50	C	clays over till	
			BC	50 to 100+	CL		

- Solonetzic soils (with hardpan B horizons) are less permeable than Luvisolic soils

9.3.1.3 Soil Sampling

- composite samples of L-H and Ap horizons were collected from the pit vicinity
- other horizons were sampled in pits

9.3.2 Comparison of Valleyview Area Soils with Teepee Creek Soils

Soils in the Valleyview area have less organic matter in surface horizons than soils in the Teepee Creek area and are therefore gray coloured rather than black or dark gray.

Soils sampled in the Valleyview area are mostly Gray luvisol and Gray solonetzic soils developed on glaciolacustrine clays (sometimes called lacustrotill). These soils usually fall within the group referred to by the Donnelly soil name.

The A horizons of the soils in the Valleyview area will have similar or possibly somewhat more rapid infiltration and permeability rates than in the Teepee Creek area. The B and C horizons of the soils on glaciolacustrine clays in both areas should be similar provided of course that solonetzic B horizons and luvisolic B horizons are compared with their equivalents.

9.4 TYPICAL PLANT SPECIES FOUND IN TREMBLING ASPEN COMMUNITIES

Tree Layer

trembling aspen	(*Populus tremuloides*)
balsam poplar	(*Populus balsamifera*)
white spruce	(*Picea glauca*)
black spruce	(*Picea mariana*)

Small Tree - Tall Shrub Layer

willows	(*Salix* species)
red osier dogwood	(*Cornus stolinifera*)
saskatoon-berry	(*Amelanchier alnifolia*)

Low Shrub Layer

wild roses	(*Rosa* species)
lowbush cranberry	(*Viburnum edule*)
snowberry	(*Symphoricarpus albus*)
Canadian buffalo-berry	(*Shepherdia canadensis*)
wild red raspberry	(*Rubus strigosus*)
wild gooseberry	(*Ribes oxyacanthoides*)

Herb Layer

Canada bunchberry	(*Cornus canadensis*)
wild vetch	(*Vicia americana*)
wild pea-vine	(*Lathyrus ochroleucus*)
dewberry	(*Rubus pubescens*)
northern bedstraw	(*Galium boreale*)
wild strawberry	(*Fragaria glauca*)
fireweed	(*Epilobium angustifolium*)
Lindley's aster	(*Aster ciliolatus*)
wild lily-of-the-valley	(*Maianthemum canadense*)
common pink wintergreen	(*Pyrola asarifolia*)
one-sided wintergreen	(*Pyrola secunda*)
twin-flower	(*Linnaea borealis*)
marsh reed-grass	(*Calamogrostis canadensis*)
slender wheat-grass	(*Agropyron trachycaulum*)
hairy wild rye	(*Elymus innovatus*)

Moss-Lichen Carpet

Amblystegium serpens
Brachytecium salebrosum
Ceratodon purpureus
Dicranum species
Plagiothecium laetum
Pylaisiella polyantha
Cladina species
Cladionia species
Hypogymnia physodes
Parmelia sulcata
Parmeliopsis ambigua
Parmeliopsis hyperopta
Peltigera apthosa
Peltigera canina

9.5 $\delta^{34}S$ VALUES AND SULPHUR CONCENTRATIONS FOR SO_2 AND SUSPENDED PARTICULATE MATTER SAMPLED IN THE VALLEYVIEW AREA, ALBERTA. 1980.

Table 5. $\delta^{34}S$ values and sulphur concentrations for SO_2 and suspended particulate matter sampled at the Dallman Farm, approximately 15 km NNW of Valleyview, Alberta, 1980 27 May to 07 June.

Sampler	Time	SO_2		TSP	
		$\delta^{34}S$	[S](10^{-6} g/m^3)	$\delta^{34}S$	[S]10^{-6} g/m^3
NNE	1953	18.1	0.4	17.7	1.1
ENE	226		6.1	19.2	2.0
ESE	130	20.3	3.5	17.3	2.6
SSE	374	21.1	4.6	17.2	3.1
SSW	862	26.0	1.1	18.0	0.7
WSW	1744	20.0	2.6	17.0	4.5
WNW	4155	22.0	1.1	15.5	0.3
NNW	6730	18.5	0.2	12.1	0.2
Low	117	24.3	39.1	22.1	2.9

Table 6. $\delta^{34}S$ values and sulphur concentrations for SO_2 and suspended particulate matter sampled at the Mêlenius Farm, approximately 14 km N of Valleyview, Alberta, 1980 June 07 to June 14.

		SO_2		Particulates	
Sampler	Time	$\delta^{34}S$	[S](10^{-6} g/m^3)	$\delta^{34}S$	[S]10^{-6} g/m^3
SSE	1352	23.6	P1 & 2[a]	13.9	0.7
			P4 & 5	14.0	0.8
SSW	887				
WSW	2324		P1 & 2	11.55	0.4
			P3	24.2	0.2
			P5	19.0	0.3
WNW	2320	22.0	P1	15.2	0.2
			P2	26.1	0.2
			P3	22.6	0.2
			P4	18.0	0.2
NNW	1961		P1 & 2 & 3	12.8	0.3
			P4 & 5	9.3	0.4

[a] Different aerodynamically-sized fractions, P1 largest.

Table 7. $\delta^{34}S$ values and sulphur concentrations for SO_2 and suspended particulate matter sampled at the Gourlay Farm, approximately 14 km N of Valleyview, Alberta, 1980 June 18 to 24.

		SO_2		Particulates		
Sampler	Time	$\delta^{34}S$	[S](10^{-6} g/m^3)		$\delta^{34}S$	[S](10^{-6} g/m^3)
ESE	452		1.0		NE	
SSE	1556	22.2	0.8	P1 & 2[a]	13.3	0.4
				P3	15.5	0.2
				P4 & 5	14.4	0.4
SSW	3077	20	.3	P1	14.0	0.2
				P5	11.3	0.1
WSW	1849			P1	14.0	0.3
				P2 & 3	15.4	0.4
				P4	16.5	0.4
				P5	16.4	0.2

[a] Different aerodynamically-sized fractions, P1 largest.

Table 8. $\delta^{34}S$ values and sulphur concentrations for SO_2 and suspended particulate matter sampled at the Hallbisky Farm, approximately 15 km W of Valleyview, Alberta, 1980 June 24 to July 03.

		SO_2		Particulates		
Sampler	Time	$\delta^{34}S$	[S](10^{-6} g/m^3)		$\delta^{34}S$	[S](10^{-6} g/m^3)
SSE	1731	11.2	0.3	P1[a]	13.9	0.5
				P2	3.2	0.2
				P3	0.9	0.4
				P4	6.6	0.4
				P5	4.3	0.5
SSW	846	1.2	0.3			NE
WSW	1141	*	0.4	P1-4	4.0	1.0
				P5	-9.4	0.5
NNW				P1	4.1	0.2
				P3	7.4	0.2
				P5	6.2	0.1

[a] Different aerodynamically-sized fractions, P1 largest.

Table 9. $\delta^{34}S$ values and sulphur concentrations in SO_2 and suspended particulate matter sampled at the Halibisky Farm, approximately 15 km W of Valleyview, Alberta, 1980 November 09 to 19.

		SO_2		Particulates		
Sampler	Time	$\delta^{34}S$	[S](10^{-6} g/m^3)		$\delta^{34}S$	[S](10^{-6} g/m^3)
NNE	245	1.0	1.3			
ENE	112	6.3	3.1			
SSE	2102	10.3	0.4	P1-3[a]	8.7	0.4
				P4-5	7.7	0.4
SSW	1069	7.4	0.6	P1-3	7.4	1.2
				P4-5	7.1	0.6
WSW	811	4.7	0.3	P1-3	9.1	4.9
				P1-2	1.3	0.2
				P3	2.0	0.6
				P4-5	0.7	1.8
				P4-5	1.3	0.4
WNW	3758	7.3	0.2	P1-4	8.2	0.3
				P5	7.0	0.3
NNW	5018	7.5	0.2	P1-2	8.2	0.2
				P1-2	4.01	0.4
				P3-5	8.6	0.2
				P3-5	4.4	1.0

[a] Different aerodynamically-sized fractions, P1 largest.

Table 10. $\delta^{34}S$ values and sulphur concentrations in SO_2 and suspended particulate matter sampled at the Dallman Farm, approximately 15 km NNW of Valleyview, Alberta, 1980 November 25 to 30.

		SO_2		Particulates		
Sampler	Time	$\delta^{34}S$	[S](10^{-6} g/m^3)		$\delta^{34}S$	[S](10^{-6} g/m^3)
SSE	409	25.0	0.8	P1-3[a]	13.2	1.1
				P4-5	18.4	5.0
SSW	717	21.6	1.3	P1-3	15.8	1.9
				P4-5	8.7	1.0
WNW	802	12.4	0.3	P1-3	12.7	1.3
				P4-5	8.7	0.4
NNW	452			P1-3	6.9	0.7
				P4-5	6.4	0.7

[a] Different aerodynamically-sized fractions, P1 largest.

Table 11. $\delta^{34}S$ values and sulphur concentrations in SO_2 and suspended particulate matter collected on the roof of the Provincial Building, Valleyview, Alberta, 1980 June 17 to July 11.

SO_2		TSP			
$\delta^{34}S$	[S]·(10^{-6} g/m^3)	$\delta^{34}S$	[S]·(10^{-6} g/m^3)	Starting Date	Duration (hr.)
20.5	1.7			80-06-17	48
16.6	0.6	32.6	0.3	80-02-19	48
18.3				80-06-24	72
13.9	0.3	13.5	0.3	80-01-27	96
18.4				80-07-01	72
17.6				80-07-04	168

Table 12. $\delta^{34}S$ values and sulphur concentration for SO_2 and total suspended particulates collected on the Dallman Farm, approximately 15 km NNW of Valleyview, Alberta, 1980 June 19 to July 19.

SO_2		TSP			
$\delta^{34}S$	[S]·(10^{-6} g/m^3)	$\delta^{34}S$	[S]·(10^{-6} g/m^3)	Starting Date	Duration (hr.)
17.7	2.1	19.2	0.6	80-05-18	24
	0.8	18.6	1.1	80-06-20	24
15.1	0.3	14.7	0.3	80-06-21	96
13.2	0.1	20.4	0.2	80-06-25	96
15.6	0.2	11.5	0.1	80-06-29	96
19.7	0.2	NE	0.1	80-07-01	48
16.1	1.7	[a]18.2 & 17.8	1.1	80-07-03	48
17.9	1.0			80-07-05	48
14.5	0.3			80-07-07	48
		16.9	0.2	80-07-09	48
18.7	0.3	16.8	0.4	80-07-11	48
		17.2	0.4	80-07-13	48
22.0	0.4	14.7	0.4	80-07-16	72

[a] Replicate values

9.6 SULPHUR CONCENTRATION AND $\delta^{34}S$ RESULTS FOR BULK RAIN SAMPLES COLLECTED IN THE VALLEYVIEW AREA, ALBERTA, SUMMER 1980.

Table 13. Sulphur concentration and $\delta^{34}S$ results for bulk rain samples[a] collected in the Valleyview area, Alberta, summer 1980.

Location	$\delta^{34}S$ °/oo	Concentration (ppm)
Melenius Farm	12.9	0.6
Radomske Farm	16.4	1.4
Dallman Farm - July	11.4, 11.5[b]	0.7
- August	9.3	0.9
Gourlay Farm	16.5	0.3
Dumo Farm	14.2	1.6
Loewen Farm	20.6	0.3
Bitz Farm	15.4	1.6

[a] Composite wet and dryfall samples
[b] Replicate values

9.7 SULPHUR SIRA RESULTS FOR SURFACE WATER SAMPLES COLLECTED IN THE VALLEYVIEW AREA, ALBERTA, SUMMER 1980.

Table 14. Sulphur SIRA results for surface water samples collected in the Valleyview area, Alberta, summer 1980.

Site	Location	$\delta^{34}S$ Del.	PPM[b]
1	Sturgeon Lake at Young's Point Provincial Park	-5.5, -6.4[a]	>1
2	Sturgeon Creek at Highway 34	-9.8	2.5
3	Site 2 (natural pond)	19.2	>40
4	Site 15 (natural pond)	12.3	>25
5	Site 16 (dugout)	16.1	>35
6	4 km E of Site 16 (dugout)	0.5, 1.4[a]	5
7	Site 5 (dugout)	-4.2	5.8
8	A. Dallman Farm (dugout)	-3.4[a]	8
9	.8 km W of E. Dallman Farm (dugout)	-5.9, -10[a]	5.6
10	1.6 km W of E. Dallman Farm (dugout)	-6.4, -6.9[a]	10
11	E. Dallman Farm (dugout)	-4.1, -4.6[a]	3.7
12	.8 km SW of Site 12 (dugout)	1.1	>25
13	1 km NW of Site 12 (dugout)	-10.2, -10.3[a]	4
14	1 km E of Site 12 (dugout)	-4.4, -4.7[a]	3

[a] Replicate values.
[b] Concentration measured for single aliquot prior to SIRA analysis.

9.8 pH, SULPHUR CONCENTRATIONS, AND SIRA RESULTS FOR SOILS, VALLEYVIEW AREA, ALBERTA, SUMMER 1980.

Table 15. pH, sulphur concentrations, and SIRA results for soils, Valleyview, Alberta, Summer 1980.

Site	Horizon	cm	Sol ppm	Sol $\delta^{34}S$	Total ppm	Total $\delta^{34}S$	pH	Distance and Direction from Stack (km)
1	LFH	5 to 0	18	12.9	1479	9.3		3.2 NNE
	Ahe	0 to 5	4	0.9			6.8	
	Ae	5 to 12	9	6.6				
	AB	12 to 35	10	5.4			5.5	
	Bt	35 to 60+	5	1.1			4.5	
2	LFH	3 to 0	36	18.3	554	9.7		0.5 E
	Ae	0 to 5	24	5.2			6.8	
	AB	5 to 30		1.0			5.5	
	Bt	30 to 70	11	0.3			5.5	
	BC	70 to 110+	50	-0.5			6.2	
3	LFH	5 to 0	27	8.4	1294	7.3		4.0 SE
	Ae	0 to 10	14	5.9				
	AB	10 to 30	23	-5.1			6.0	
	Bt	30 to 65	10	-0.4			5.5	
	Ck	65 to 110+	117	-5.5			6.9	
4	LFH	5 to 0	284	3.0	1220	1.8		8.7 E
	Ae	0 to 15	5	-1.5			4.0	
	Bntgj	15 to 35	48	-10.6			4.9	
	BCg	35 to 70					6.1	
	Csak	70 to 160+	143	-7.4			7.1	
5	Ap	0 to 20	27	-12.0			6.4	9.3 E
	Bntgj	20 to 40	22	-10.3			5.7	
	BC	40 to 60	149	-12.0			7.2	
	Csak	60 to 110+	17	-11.5			7.4	

continued ...

Table 15. Continued.

Site	Horizon	cm	Sol ppm	Sol $\delta^{34}S$	Total ppm	Total $\delta^{34}S$	pH	Distance and Direction from Stack (km)
6	Ap	0 to 15	13	9.1			5.0	8.9 ENE
	AE	15 to 18					5.0	
	Bnt	18 to 40	9	-0.5			5.0	
	BC	40 to 80	20	5.2			7.1	
	Csk	80 to 110+	41	-9.6			8.0	
7	LFH	5 to 0	36	10.7	1337	6.7		9.3 ENE
	Ae	0 to 10	7	4.9			5.0	
	AB	10 to 20	28	11.7			5.0	
	Bt	20 to 60	9	7.3			4.5	
	BC	60 to 100+	4	-3.6			5.0	
8	Ap	0 to 15	7	-1.5			6.0	10.5 E
	Btgjnj	15 to 45	13	-5.8			6.0	
	BCg	45 to 75	28	-10.6			6.0	
	Ckg		355	-12.5	370	-8.8	8.0	
9	LFH	5 to 0	31	7.9	1220	3.8		10.9 E
	Ahe	0 to 5	4	3.7			5.9	
	Ae	5 to 20	3	1.4			6.0	
	Btgjnj	20 to 50	29	-3.2			5.5	
	BCg	50 to 85	90	-7.8			5.5	
	Ckg	85+	300	-9.1			8.0	
10	Ap	0 to 20	5	-2.6			6.5	12.9 E
	Btgjnj	20 to 50	13	-11.0			6.0	
	BCg	50 to 80	20	-12.7			6.9	
	Ckg	80 to 110+	65	-11.4			8.0	

continued ...

Table 15. Concluded.

Site	Horizon	cm	Sol ppm	Sol $\delta^{34}S$	Total ppm	Total $\delta^{34}S$	pH	Distance and Direction from Stack (km)
11	LFH	5 to 0	7	2.9	739	1.1	6.0	13.0 E
	Ae	0 to 15	4	3.4			5.2	
12	Ap	0 to 20	6	-2.8			5.0	17.7 E
	Btnj	20 to 55	30	-12.4			6.8	
	Csk	55 to 100+	15	-14.1			8.0	
13	LFH	5 to 0	9	4.2	1442	1.2	6.0	8.9 SW
	Ae	0 to 10	2	0.4			6.5	
	AB	10 to 15					6.0	
	Bt	15 to 60	31	-6.5			5.6	
	BC	60 to 75	61	-6.0	185	-3.4	5.6	
	Ck	75 to 110+	67	-5.9			7.5	
14	Ap	0 to 25	14	-4.4			7.0	13.7 SW
	Aeg	25 to 28					6.5	
	Btg	28 to 50	26	-5.8			5.5	
	BCg	50 to 75	14	-6.2			5.5	
	Ckg	75 to 100	74	-6.7			7.1	
15	LFH	3 to 0	16	21.3	961	12.3		1.4 E
	Ahe	0 to 2					5.5	
	Ae	2 to 20	3	7.9			6.0	
	Bt	20 to 50	11	-2.2			5.5	
	BC	50 to 100+	46	-2.4	148	5.9	7.5	

9.9 BUFFERING CAPACITIES OF SOILS, VALLEYVIEW AREA, ALBERTA, SUMMER 1980.

Table 16. Buffering capacities of soils, Valleyview, Alberta, summer 1980.

Site	Horizon	meq. H^+					
		0	2	4	8	16	24
1	AB	5.5	4.3	3.9	3.5	2.9	2.4
2	AB	5.5	5.3	5.5	5.4	4.8	3.7
	AE	6.8	5.6	5.4	4.9	3.5	2.5
	BC	6.2	5.3	5.0	5.0	4.5	3.9
3	AB	6.0	5.2	5.1	4.1	2.9	2.5
	BT	5.5	5.3	5.3	5.3	4.5	3.7
	CK	6.9	6.2	6.2	5.9	5.7	5.6
4	AE	4.0	3.6	3.3	3.0	2.6	2.3
	BNT	4.9	4.5	4.2	3.9	3.4	3.1
	CSK	7.1	7.8	7.5	7.6	7.7	7.9
5	AP	6.4	5.8	5.5	4.3	3.5	3.3
	BC	7.2	6.8	6.5	4.2	3.7	3.2
	CSK	7.6	7.5	7.4	7.4	7.3	7.3
6	AP	5.0	4.1	4.2	3.4	2.9	2.7
	BNT	5.0	4.0	3.9	3.8	3.1	2.8
	BC	7.1	7.4	7.3	7.1	6.4	6.2
	CSK	8.0	8.2	8.2	8.1	8.0	7.6
7	AE	5.0	3.9	3.5	3.1	2.7	2.4
	AB	5.0	3.9	3.5	3.5	3.2	2.7
8	AP	6.0	4.5	4.1	3.6	3.1	2.8
	BTGJNJ	6.0	4.2	3.9	3.7	3.3	3.0

continued ...

Table 16. Concluded.

	BCG	6.0	4.1	3.9	3.6	3.2	3.0
	CKG	8.0	7.1	7.1	7.6	8.1	8.3
9	AHE	5.9	5.2	4.5	3.8	3.2	3.0
	BC	5.5	4.6	4.1	3.5	3.2	2.9
	CK	8.0	7.5	7.4	7.4	7.3	7.2
11	LH	6.0	5.9	5.8	5.5	5.4	4.6
12	AP	5.0	4.4	4.3	3.8	3.3	2.8
	BTNJ	6.8	4.2	4.0	3.8	3.3	3.0
	CSK	8.0	7.1	7.3	7.5	7.7	7.8
13	BC	5.6	4.7	4.5	3.8	3.2	3.0
	CK	7.5	7.4	7.3	7.2	7.2	7.1
15	BT	5.5	4.2	3.9	3.5	2.9	2.7

9.10 SULPHUR SIRA RESULTS OF THE ANALYSIS OF *PARMELIA SULCATA* AND OTHER EPIPHYTIC LICHENS, TREMBLING ASPEN FOLIAGE, GROUND LICHENS AND MOSSES, FERTILIZERS, AND CROPS IN THE VALLEYVIEW AREA, ALBERTA.

Table 17. Sulphur SIRA results for *Parmelia sulcata* and other lichens growing on trembling aspen in the Valleyview area, Alberta, summer 1980.[a]

Site	Sol S $\delta^{34}S$	Sol S Conc	TS $\delta^{34}S$	TS Conc	Elev. (M)	Elev. (Ft.)	Date	Distance and Direction from Stack (km)
1				216	884	2900	80-09-04	3.2 NNE
2			8.3	733	792	2600	80-09-04	0.5 E
3	14.8	244	15.2	1423	731	2400	80-09-04	4.0 SE
4	21.4	148	11.9	1164	747	2450	80-09-04	8.7 E
c	12.5	84	11.0	862			80-09-04	8.7 E
5					753	2470	80-09-04	9.3 E
6					777	2550	80-07-02	8.9 ENE
7	16.6	59	14.6	338	777	2550	80-07-02	9.3 ENE
c	16.2	88	15.0	474			80-07-02	9.3 ENE
8					747	2450	80-07-02	10.5 E
9	21.0	144	16.0	690	747	2450	80-07-02	10.9 E
c	22.8	50	8.5	819			80-07-02	10.9 E
b			16.2	1404			80-07-02	10.9 E
10					701	2300	80-07-02	12.9 E
11	19.3	77	11.6	1380	701	2300	80-07-02	13.0 E
c	11.3	46	12.7	776			80-07-02	13.0 E
12					671	2200	80-07-02	17.7 E
13	13.7	277	15.6	1164	655	2150	80-07-03	8.9 SW
14	14.0	107	10.5	1035	716	2350	80-07-03	13.7 SW
15[c]	10.4	168	15.5	560			80-07-03	1.4 E
c	22.1	101	16.2	690	792	2600	80-09-04	1.4 E
16[d]	17.2	52	9.8	690			80-09-04	8.0 E
17[d]	17.3	78	6.5	862	655	2150	80-09-05	2.0 SSE
d	18.0	150	8.1	949			80-09-05	

[a] Missing data due to low sulphur content or losses during preparation.
[b] *Physcia airpolia*
[c] *Hypogymnia physodes*
[d] *H. physodes* - *P. sulcata* mix

Table 18. Sulphur SIRA results for trembling aspen collected in the Valleyview area, Alberta, summer 1980.[a]

Site	Soluble Sulphur		Total Sulphur		Date	Location from Stack (km)
	$\delta^{34}S$	ppm	$\delta^{34}S$	ppm		
1	15.0	206	5.0	296	81-09-04	3.2 NNE
2	-8.0	23	14.9	961	80-09-04	0.5 E
3	4.5	129	4.0	961	80-09-04	4.0 SE
7	10.1	58	3.7	1294	80-07-02	9.3 E
9	-3.6	24	1.1	1479	80-07-02	10.9 E
11	3.5	68	-3.7	1774	80-07-02	13.0 E
13		15	-5.6	481	80-07-03	8.9 SW
14	-2.5	66	-6.6	949	80-07-03	13.7 SW
15			4.1	259	80-07-03	1.4 E
	8.5	62	14.6	2328	80-09-04	1.4 E
16	8.9	49	6.6	1737	80-09-04	8.0 E
17			3.7	887	80-09-04	2.0 SSE

[a] Missing data due to low sulphur content or losses during preparation.

Table 19. Sulphur SIRA data for ground lichens and mosses in the Valleyview area, Alberta.[a]

Site	Species	Soluble S °/oo	Soluble S ppm	Total S °/oo	Total S ppm	Location from Stack (km)	Date
1	*P. schreberi*[b]			13.3	554	3.2 NNE	80-09-04
16	*P. schreberi*			7.1	850	8.0 E	80-09-04
2	*Cladonia* sp.		154	17.5	1220	0.5 E	80-09-04
16	*Cladonia* sp.	10.7	131	12.1	776	8.0 E	80-09-04
4	*P. apthosa*[c]	13.5	85	11.3	776	8.7 E	80-09-04
17	*P. apthosa*		42	10.4	1257	2.0 SSE	80-09-05

[a] Missing data due to low sulphur content or losses during preparation.
[b] *P = Pleurozium*
[c] *P = Peltigera*

Table 20. Sulphur SIRA results for trace contaminant sulphur in commercial bulk fertilizers,[a] commonly used in the Valleyview area, Alberta.

N-P-K	$\delta^{34}S$ Range
COOP 26-13-0	17.9 to 18.3
COOP 11-51-0	17.7 to 17.9
COOP 34-0-0	12.6
COOP 11-48-0	15.3 to 15.9
ESSO 11-48-0	10.2 to 10.3

[a] These fertilizers are composed of nitrogen, phosphorus, and potash.

Table 21. Sulphur SIRA data for crops in the Valleyview area, Alberta.

Site Location	Species	Total S ‰	Total S ppm	Location from Stack (km)
32-71-22 W5M	Rapeseed	-2.8	1882	8.9 km EBE
6-72-22 W5M	Rapeseed	-6.9	3881	8.9 km ENE
32-71-22 W5M	Wheat	-3.1	1220	9.3 km E
12-72-22 W5M	Rapeseed	-10.9	2070	17.0 km ENE
32-71-21 W5M	Rapeseed	-5.8	2588	21.0 km E
32-71-21 W5M	Oats	-5.9	629	21.0 km E
16-72-21 W5M	Rapeseed	-16.5	2329	23.0 km NE
16-72-21 W5M	Oats	-12.5	370	23.0 km NE
20-72-21 W5M	Wheat	-8.6	702	23.0 km NE
10-72-21 W5M	Rapeseed	-9.2	2218	28.0 km NE